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Handsheet and fourdrinier testing of titanium dioxide in filled paper

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HANDSHEET AND FOURDRINIER TESTING OF TITANIUM DIOXIDE IN FILLED PAPER

by

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(date)

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NOMENCLATURE AND GLOSSARY

$C_{0.89}$ - Tappi Opacity - The ratio expressed as a percentage of the reflectance of a single sheet backed by a black cavity to the reflectance of the same sheet backed by a white body having an absolute reflectance of 0.89.

R_g - Reflectance of background to which colorant layer is applied.

R - Reflectance of layer with background of reflectance R_g.

R_∞ - Brightness - Reflectance of layer so thick that further increase in thickness fails to change the reflectance.

S - Coefficient of scatter, increase of reflectance with thickness of a very thin layer for diffusely incident radiant energy.

K - Coefficient of absorption, decrease of transmittance with thickness of a very thin layer for diffusely incident radiant energy.

x - Thickness of layer.

R_o - Reflectance of layer with ideal black background R_g = o.

$R_{0.98}$ - Reflectance of layer with background of reflectance 0.98.

Basis Weight - The weight in pounds of a ream of paper cut to a specific size.

Consistency - The percentage, by weight, of airdry or ovendry fibrous material in a stock or stock suspension.

Freeness - A measure of the rate with which water drains from a pulp suspension through a wire mesh screen or a perforated plate. Parameter for measuring degree of beating or refining of pulp.

Furnish - The mixture of various materials that are blended in the stock suspension from which paper is made.

Calender - A set of horizontal rolls with chilled hardened surfaces resting one on the other on a vertical bank at the end of the paper machine. The paper is passed between these rolls to increase the smoothness and gloss of its surface.

Calendering - The operation of finishing a sheet of paper by passing through a calender.

Opacity - The property of a sheet which obstructs the passage of light and prevents one from seeing through the sheet.

Optical Efficiency - Scattering power per unit of pigment in a sheet of paper. Scattering coefficient is a measure of optical efficiency.

ABSTRACT

An experimental program was conducted to study the effect of alum concentration, rosin size concentration, type water, pH of papermaking system, pH and time of reaction, and order of additive addition on the optical efficiency and retention of TiO_2 on a laboratory Fourdrinier and handsheet machine and show correlations between these two papermaking systems.

The variables exhibiting most significant effects were alum concentration, type water and reaction time.

The degree of correlation between the two systems was dependent on reaction time and alum and rosin size concentration.

The complicated interactions detected indicate that further work is needed in the development of a meaningful laboratory paper filler test method.

INTRODUCTION

I. The Papermaking Process

The manufacture of paper is one of the world's oldest and largest industries. Originally it was an art in which the skills and "know-how" were passed on in families from one generation to the next. As in other industries, in recent years, increased consideration has been given to the scientific approach to the development of improved and new products.

There are three types of plants in the paper industry: integrated mills in which finished paper is manufactured from wood and other raw materials; mills that start with pulp manufactured at another location, and converters that do not manufacture paper but treat, coat, or finish papers.

The fibers that compose paper pulps come from several sources. These include naturally occurring fibers such as cotton that can be used directly and those fibers that are obtained by separation and treatment processes from wood and other materials. The most important source of fibers is wood. The production of wood pulp could include a discussion of forestry, logging or harvesting of the trees, cutting, chipping or grinding, and the various mechanical and chemical treatments. This is beyond the scope of this work and additional information can be found elsewhere.[17]

Paper manufacture consists of the separation, purification and treatment of fibers; the incorporation of various other ingredients with the fibers; the formation and drying of sheets; and various treatments and processing of the sheets. The fibers

are usually of vegetable origin, generally cellulose from wood. If the production of the fiber is a part of the paper manufacturing plant, that is, it is an integrated mill, the fibers may be in the form of dispersed wood pulp. However, in many cases the pulp is obtained in the form of dry baled sheets. Repulping it in water is the first step of paper manufacture.

Irrespective of the type of paper, its preparation from pulp can be considered to involve a four-stage process:

1. Preparation of the stock - furnishing, beating and refining.
2. Forming of the sheet.
3. Removing water and drying of the sheet.
4. Conversion - finishing and coating of paper.

A. Preparation of Paper Stock

In order that the cellulose fibers in the pulp may be formed into paper, any clusters of fibers must be dispersed and broken up into short individual fibers. The walls and ends of the fibers must be frayed into fine hair-like segments then hydrated and gelled. The processes by which these effects are accomplished are usually designated as pulping, beating and refining.

Other constituents, fillers, alum, rosin size, starch and glues, of the paper are incorporated during the preparation of the stock. There is considerable variation as to the order of additions and where, when and how the different ingredients are added. Again procedures vary with specific ingredients, kinds of stock, types of equipment, kinds of paper, preferences and "know-how"

of the manufacturer. Additions may be in the initial repulping process, and in various stages of beating and refining. In the case of some papers, certain ingredients may be added during the manufacture of the sheet.

B. Formation and Drying of the Paper Sheet

The second step in the manufacture of paper is the formation of sheet from fiber suspensions. Paper sheets originally were handmade by extracting the fiber-water stock from a tub by dipping with a rectangular wood framed wire-mesh sieve. The first modern papermaking machine was invented by a Frenchman, Nicholas-Louis Robert, and its development was financed by two London stationers, Henry and Sealy Fourdrinier. It consisted of a rotating wire-mesh belt on which a continuous sheet of paper was formed. Although there have been extensive modifications, revisions, improvements and expansions of the original machine, any paper machine using a continuous wire-mesh belt is called a Fourdrinier.

In modern Fourdrinier paper machines, the sheet not only is formed but the water is removed and the dried sheet calendered and in some cases sized or coated. Fourdrinier machines are among the most massive machines found anywhere in modern industry. They are up to a city block in length, have screens up to 300 inches wide traveling at speeds to produce over 3,000 linear feet of paper per minute. A laboratory scale model of a Fourdrinier is shown in Figures 5, 6, and 7.

Paper is made from the previously described fiber stock, by passing the stock (approximately 3% solids) through mechanical

cleaners (centrifuges and/or suction screens with narrow slits to remove dirt or other foreign materials). It is then diluted to 1/10 to 2 percent solids and fed uniformly to the full width of the Fourdrinier screen through a rectangular slit. The rate of stock deposition on the screen in relation to the speed of the screen, shaking and other controls are used to vary the thickness and weight of the product. While on the screen, water is removed by draining assisted by contact with the rolls supporting the wire. Further water is removed by suction boxes and the suction couch roll. The couch roll is the driving roll for the wire and is where the paper leaves the wire to go to the presses. (Actually the Fourdrinier part of the papermaking machine ends with the paper going to the presses.)

The paper web is taken from the wire to a wool felt which carries it through roll presses (wringers) which remove more of the water, press down the surface and densify the paper. After the presses, the paper which still contains 50 or more percent moisture passes under its own support to dryers. The standard paper dryer is a hollow 4 or 5 foot diameter cast iron cylinder of uniform wall thickness with the outer wall machined to a fine smooth finish. The drums are normally heated by steam. There are a large number of these, in some machines well over 100. As the paper passes over these huge steam heated drums, cotton or asbestos felt is held against them to increase the drying efficiency. The water in the paper is gradually reduced to the desired moisture content, usually 4-1/2 to 6 percent.

The paper goes from the dryers to the calenders. These are vertical stacks of extremely fine grain chilled cast iron rolls. The rolls are in contact and the paper passes into the nip of roll one and roll two, then into the nip of rolls two and three, etc. The only driven roll is the bottom roll; the rest rotate by friction. The bottom roll is the largest and the roll just above it is smaller but still slightly larger than the others, which all have the same diameter. Doctor blades are mounted on each roll to keep them clean and to prevent the sheet from running up the rolls. Papermaking is a continuous process from the head-box to the calender. Paper from the calenders is usually wound on reels.

II. Pigmentation of Paper

Fillers, which include pigments, constitute the major portion of the non-fibrous materials in paper. The incorporation of fillers into paper enhances optical properties and produces smoothness and more uniform surfaces for printing. Other sheet properties which may be controlled by the type of filler are ink penetration, texture or softness, bulk or caliper, dimensional stability and the ease of attaining a given level of smoothness through calendering. The degree to which these properties are developed depends on the chemical composition, particle size, particle shape, surface area and refractive index of the fillers.

Clay is an all-purpose pigment and serves as the major filler in paper. Clays are produced in varying size and shapes and are generally adequate for the majority of properties. However, for the attainment of the high opacity desired in many book and other quality papers, the use of titanium dioxide is generally warranted. TiO_2 has a crystal unit cell in which the titanium and oxygen atoms are tightly bound with small distances between them. Because of this tight structure, TiO_2 has a high refractive index relative to other commercially available materials. It is available in two crystal forms, anatase having a refractive index of 2.55 and rutile having a refractive index of 2.71. In this report we will be concerned only with the anatase crystal form.

Table I lists the refractive indices of common materials found in a sheet of paper.

Table I

Refractive Indices of Materials Used in Paper

Anatase TiO_2	2.55
Clay	1.55
Cellulose Fiber	1.55
Rosin Size	1.55
Sodium Alumina Silicate	1.55
Silica Dioxide	1.46
Air	1.00

The effect of using TiO_2 instead of clay for the improvement of optical properties can be demonstrated by the Fresnel Equation, which shows the dependency of light reflected on the difference in the refractive indices of two substances in contact:

$$R = \frac{(N_2 - N_1)^2}{(N_2 + N_1)} \qquad (1)$$

Where:

R = Amount of light reflected

N_1 and N_2 = Refractive indices of materials in contact

For clay-air:

$$R = \frac{(1.55 - 1.00)^2}{(1.55 + 1.00)} = 0.047$$

For TiO_2-air:

$$R = \frac{(2.55 - 1.00)^2}{(2.55 + 1.00)} = 0.19$$

This increase in the amount of light reflected is the basic reason for using TiO_2 as a paper filler. With this higher reflectance, there will be less light transmitted, hence higher opacity.

Paper manufacturers are under increased pressure to reduce paper weight as rising postal rates, which are based on weight, have meant a cumulative increase in magazine publishers costs of

over 22 percent, between 1968 and 1970, unless the publishers resort to lighter weight papers. Many publishers who previously used 40-pound or 38-pound paper have found a drop to 36 pounds offsets a great part of the increased postal charge. Some are currently seeking to reduce the weight still further to 34 pounds, and it is likely that the 1970 increment of the postal rate increase will spark a demand for 32-pound paper. If this progressive decrease is achieved, the publishers' mailing costs in a typical instance can be held down to about what they were in 1967 before the higher postal charges went into effect. Many paper mills have found this trend to lighter papers costly due to the difficulties in handling and running lightweight paper.

One of the basic methods of improving the overall profit picture of the paper manufacturer is to use titanium dioxide more efficiently. By using a minimum amount of TiO_2 for maintenance of optical properties the paper manufacturer will minimize physical strength degradation. Handling will not suffer as the incorporation of pigments in paper reduces the strength of the paper.

It should also be noted that the price differential between TiO_2 and other commercially available fillers is quite pronounced: TiO_2 at 23.5¢ per pound, SiO_2 at 7¢ per pound and the clays ranging from 1.5¢ per pound to 3.5¢ per pound.

Since TiO_2 is the most costly pigment used in the production of most fine papers, the papermaker must optimize its use; i.e., develop highest optical efficiency and maximum retention

properties using a minimum of material. These properties will be fully discussed later in this report.

The question arises as to what methods are at the disposal of the papermaker to determine how to optimize his use of TiO_2. These methods include:

1. Plant Tests - In plant tests there is general lack of control of variables being studied. The possibility exists of producing off-grade paper in an experimental test program. Plant tests can prove costly because of high production rates and time needed to reach steady state on commercial equipment. Such tests often result in lost time and wasted paper.

2. Laboratory Fourdrinier - Simulation of commercial equipment, high speed differences eliminates the possibility of studying fluid dynamics.

3. Handsheet Machine - This method is the least costly for studying papermaking variables. A recent survey by the Technical Association of Pulp and Paper Industry expressed a need by paper manufacturers for a suitable test method on this apparatus for evaluating fillers.

The purpose of this work has been to study the effect of common papermaking variables on the optical efficiency and retention properties of TiO_2 on a laboratory Fourdrinier and handsheet machine and to show correlations between these two papermaking systems. It is also hoped that experimental results will help toward a better understanding of the mechanism of pigment retention and optical efficiency in paper. Before discussing actual experimental work, background information on these properties is given.

THEORY

I. Pigment Retention

The Fourdrinier machine, for descriptive purposes, may be divided into four sections: the wet end, the press section, the dryer section and the calender section. In the wet end, the pulp flows from a headbox through a slice onto a moving endless belt of wire, called the Fourdrinier wire. The wire runs over a series of rolls or drainage blades which maintain the working surface of the wire in a plane. In the manufacture of paper, some of the incoming pigments to the Fourdrinier is not retained in the sheet but passes through the Fourdrinier wire along with most of the water used for suspending the fiber and pigment. The water drained from the pulp is known as "white water." Approximately 75-85 percent of this white water is continuously recirculated to the headbox of the paper machine with the remainder generally passed to a saveall. A saveall is an apparatus operating on a filtration, sedimentation, flocculation, or flotation principle, used for reclaiming fibers and fillers from white water. Even with recirculation of the white water, pigment retention in most mills averages only 75-85 percent. Recirculation increases retention as the pigment retained on a first pass through a Fourdrinier wire is approximately 30 percent.

There are a number of theories on the proposed mechanism of pigment retention. Haslam and Steele[1] proposed that there are three mechanisms for pigment retention: mechanical filtration, co-flocculation and mechanical attachment. The filtration mechanism takes place when a pigment particle fails to find an opening to

pass through in the fibrous mat formed on the Fourdrinier wire during sheet formation. Coflocculation is the attachment of pigment particles to the pulp walls because of interfacial forces. Mechanical attachment is the wedging of a particle into an imperfection in the pulp fiber surface.

Stracham[2,3] stated that the precipitation of positively charged aluminum hydrates in a mass containing negatively charged colloids, such as cellulose, pigment, rosin, etc., results in the mutual coagulation of a complex containing pigment on the cellulose surface.

Rowland[4] stated that fillers may be held on fibers through the processes of surface absorption involving electrokinetic forces and trapped by filtration in the fibrous mat on the wire.

Lorenz[5] et al stated that retention was due to mechanical filtration which depended on the size of the openings in the fiber network and also by the cementing of precipitated materials.

Atsuki and Nakamura[6] indicated that mechanical entrapment was the major effect as pigments and fiber are negatively charged so that surface absorption is insignificant.

The work cited is only a cross section of findings of many investigators. Presently the most accepted theory is that a combination of mechanical filtration, coflocculation and mechanical attachment is responsible for pigment retention.

II. Optical Efficiency

Basic light scattering theory states that for optimum reflectance a particle should have an average diameter of one-half the wavelength of light, at maximum eye sensitivity, or 0.25 micron. In the manufacture of TiO_2, particle size is controlled to 0.20 micron to 0.30 micron depending on grade. Paper grade TiO_2 has an approximate (d_3) diameter of 0.25 micron for optimum optics.

The opacity of paper increases as the particle size of the pigment is decreased because smaller particles have more surface planes over which the light must pass and be refracted and reflected. Sawyer[9] points out that for particles finer than the wavelength of light, scattering increases as the particle size decreases. For particles coarser than the wavelength of light reflection decreases as particle size increases. Stutz and Pfund[10] give the correct size for maximum coverage and hiding power as approximately one-half the wavelength of the light used in receiving the material. A minimum range of 0.1 to 0.2 micron and a maximum of 0.5 micron are the extremes in particle size for maximum hiding power as fixed by the wavelength of ordinary light.

The basic problem in using TiO_2 as a paper filler is maintaining its effective size at 0.25 micron and getting adequate retention. In most paper TiO_2 will be found in a flocculated state similar to what is shown in Figure 1, a surface replica of a sheet containing TiO_2. The cluster of particles is TiO_2. This flocculated state is undesirable from the standpoint of optical efficiency. Experience has shown that flocculation generally aids

Figure 1

1 Micron

Carbon Negative Replica of TiO_2 Filled Paper
Pt-Ir Preshadowed 1:1 X17,600

retention and decreases optical efficiency. It is the objective of the papermaker to balance these two properties against cost. This report gives experimental data on different papermaking systems and shows how these properties interact.

The improvement of opacity is the most important objective of TiO_2 usage in paper. To accurately determine TiO_2's overall effectiveness, its opacifying power must be assessed independently of other factors such as fiber furnish, basis weight or brightness. Kubelka and Munk[7] developed mathematical relationships between opacity brightness and basis weight of pigment-free paper and applied them to the contribution of filler in paper. They designated "S" as the ability to reflect or scatter light (scattering coefficient) and "K" as the ability to absorb light (absorption coefficient) both per unit thickness as the thickness becomes very small.

The Kubelka-Munk Equation is:

$$R = \frac{(R_g - R\infty)/R\infty - R\infty(R_g - 1/R\infty)e\ S_x[(1/R\infty) - R\infty]}{R_g - R\infty - (R_g - 1/R\infty)e\ S_x[(1/R\infty) - R\infty]} \qquad (2)$$

Where:

R = The reflectance of any colorant layer of known absorption and scattering coefficients

R_g = The reflectance of background to which colorant layer is applied

x = Thickness of colorant layer

$R\infty$ = The reflectance of colorant layer at complete opacity

e = The Napierian logarithm = 2.71828

Note that "K", as such, does not appear in the equation. It is included, however, in the value of "R∞" which depends on the ratio of K/S as shown in Equation 3.

$$K/S = (1-R\infty)^2/2R\infty \tag{3}$$

Steele[8] developed the calculation of "S" from the reflectivity of a thick opaque pad and contrast ratio. His final equation was:

$$C_{0.98} = \frac{R_o}{R_{0.98}} = \frac{-0.98[\frac{\sinh Z}{\sinh (Y+Z)}] + 1}{+0.98[\frac{\sinh (Y-Z)}{\sinh Z}] + 1} \tag{4}$$

Where:

$C_{0.98}$ = Contrast ratio = Reflectance (R_o) of colorant layer backed by black body divided by reflectance of layer backed by a body having an absolute reflectance of 0.98 ($R_{0.98}$)

$$Z = S_x \sinh Y \tag{5}$$

$$Y = -\ln R\infty \tag{6}$$

Tappi opacity ($C_{0.89}$) is calculated from these equations by replacing 0.98 with 0.89 and using $R_{0.89}$ instead of $R_{0.98}$. Judd[9] developed a graphical diagram (Figure 2) relating the variables shown in Equation 4. Scattering power (S_x) is easily determined from opacity and reflectance determinations using this chart.

The above theory is the basis for the majority of optical evaluations of pigments in the paper industry today.

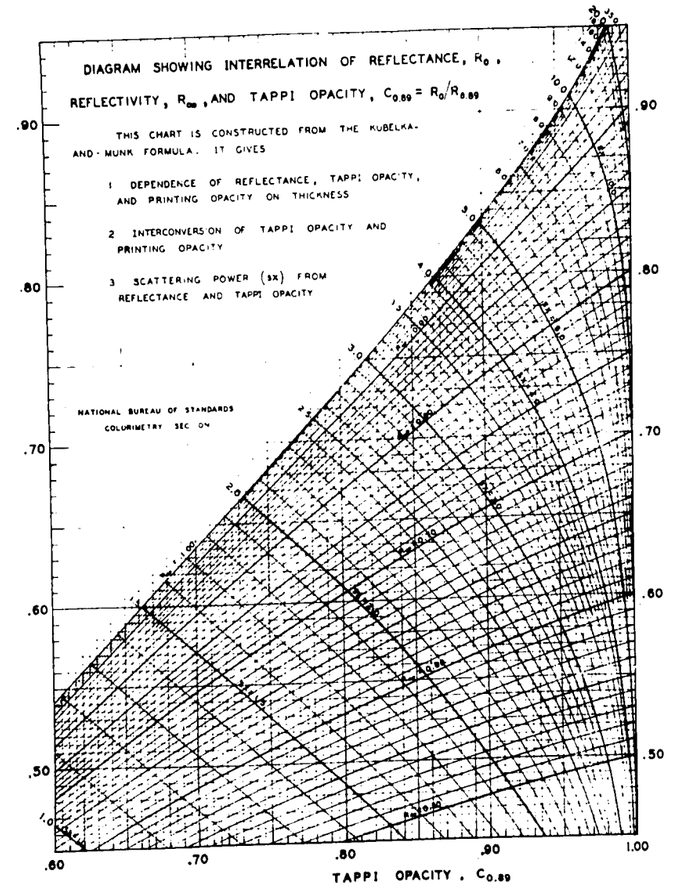


Figure 2

Judd Chart

III. Alum and Rosin Size Reaction

Two of the variables that will be considered in this report are the effects of variations in alum and rosin size concentration in the fiber-water stock.

Papermakers' alum consists of $Al_2(SO_4)_3 \cdot \chi H_2O$. The water of hydration is usually about 43 percent of total molecular weight. Its primary function in most papermaking systems is to react with rosin size and cause precipitation of a positively charged aluminum rosin complex which is absorbed on the negatively charged pulp.

Rosin size is the sodium salt of rosin in which all or part of the resin acids are neutralized. It is used in paper to aid in the resistance to liquid penetration.

The mechanism by which alum reacts with rosin size is a controversial subject. Original thinking was that a simple double decomposition reaction occurred where water resistant aluminum resinate was precipitated and soluble alkali sulfate was formed as a waste by-product. Later it was found that satisfactory sizing would occur if free rosin were present, i.e., sizing was due to precipitation of free rosin. It was also found that alum was a rosin precipitant, and the minor amount of aluminum resinate which was being formed was inactive. The literature on sizing centers around two possible theories: the ionic theory and the colloidal theory as related to free rosin.

Sieber[12] and Ostwald and Lorenz[13] stated, adhering to colloidal theory, that positively charged alumina particles, formed by hydrolysis of alum attract themselves to both negatively charged

pulp fibers and negative rosin particles forming a water repelling complex.

Evidence of the ionic theory was shown by Price[14] who concluded that alum and rosin do ionize in water and that it was the aluminum ion which was necessary for an effective rosin size precipitate. Strazdins[15] indicated that the negatively charged rosin and cellulose interact with the positive aluminum ions leading to precipitation of rosin on cellulose fiber. In this interaction, the aluminum ion exerts its positive charge. The reaction as proposed by the Hercules Company is given in Figure 3.

This report studies the effect of the kinetics of the reaction of alum and rosin size and the relationship of alum and rosin size on TiO_2's properties in paper.

FIG. 3

ALUM & ROSIN SIZE REACTIONS

$$Al_2(SO_4)_3 \rightleftharpoons 3SO_4^{=} + 2Al^{+++}$$

$$\xrightarrow{H_2O} H^+ + AlOH^{++}$$

$$\xrightarrow{H_2O} H^+ + Al(OH)_2^{+}$$

$$\xrightarrow{H_2O} H^+ + Al(OH)_3$$

$$+ RC(=O)OH \rightleftharpoons Res\,Al + H^+$$

EXPERIMENTAL PROGRAM

I. Objective

The objectives of the experimental program were to:

1. Develop further understanding of mechanisms of papermaking variables effecting the optical efficiency and retention of TiO_2 as a paper filler.

2. Determine the degree of correlation between a batch papermaking operation (Handsheet Machine) and a continuous operation (Fourdrinier) with reference to TiO_2 retention and optical efficiency.

The experimental program was conducted in two phases. The initial phase was a study of the effects of five factors on the retention and optical efficiency of TiO_2 in paper made on a handsheet machine. The factors studied were alum concentration, rosin size concentration, type water, pH of papermaking system and variations in order of addition of additives to pulp. The second phase of the program was conducted on both the handsheet and Fourdrinier. Emphasis was on the effect of the kinetics of the alum-rosin size reaction, i.e., concentration, time, and type of water on TiO_2's effectiveness as a filler. Time was studied because the determinations of degree of correlation between the handsheet and Fourdrinier was a major objective of experiment. Reasons for studying other variables will be discussed later.

II. Variables Studied in Phase I

A. Alum Concentration

Alum was added to the fiber-pigment suspensions at the 0.0 percent, 1.0 percent, 2.0 percent and 4.0 percent levels based on total solids in this program.

B. Rosin Size Concentration

Rosin size was studied at the 0.0 percent, 0.5 percent, 1.0 percent and 2.0 percent based on total solids in this experiment.

C. pH

The majority of paper mills operate in a pH range of 4.4 to 4.8 as this is the range of maximum sizing efficiency. Since sizing efficiency is of no concern in this study, a pH range of the papermaking system of 4.5 to 6.5 was studied in this test. The effect of variations in the pH of the pulp, TiO_2, rosin size and alum suspension before addition to the papermaking system was also studied. The pH was adjusted with H_2SO_4 or NaOH.

D. Order of Addition

Three different orders of addition of pigment, alum, and rosin size to pulp slurry were studied:

Order A - Size, Alum, Pigment
Order B - Pigment, Size, Alum
Order C - Alum, Pigment, Size

E. Water

The effect of water hardness was studied using (a) raw well water, and (b) demineralized water.

F. $\underline{TiO_2}$

TiO_2 addition levels based on pulp were 10.6 percent in Phase I and 11.1 percent in Phase II.

III. Experimental Equipment

The paper for this program was prepared on the Noble and Wood Handsheet Machine and the Kaemmerer Laboratory Fourdrinier Paper Machine. Both pieces of equipment are illustrated in Figures 4 to 12.

A. Noble and Wood Handsheet Machine

The Noble and Wood Handsheet Machine consists of:

1. Proportioner (Figure 4) - The proportioner is a 20-liter tank equipped with a paddle mixer. It is used as a dilution tank for pulp-pigment suspension before sheet formation with the dilution factor based on desired sheet weight.

2. Sheet Mold (Figure 5) - The sheet mold is a 12 inch by 12 inch tank which is used to produce test sheets. An aliquot portion of the pulp-pigment suspension is taken from the proportioner and poured into sheet mold where it is diluted to 0.2 percent solids in the sheet-making operation. After dilution, the suspension is agitated with the perforated plunger (Figure 5). On completion of agitation, a drain valve is pulled and sheet is formed on 100 mesh screen (Figure 5).

3. Press (Figure 6) - The press is power driven and produces sheets of 32 percent consistency. At the press the sheet and screen are placed between two sheets of felt and passed through two stainless steel rolls which are under pressure. Water from the sheet is absorbed by the felts.

4. Dryer (Figure 6) - The dryer is an electrically heated, water-filled rotating drum. It is equipped with an adjustable thermostat for temperature control and a variable speed drive. The sheet is dried at 190°F. while still supported on the screen.

The handsheet machine is a single-pass operation, i.e., any pigment, fiber or other solid which is not retained on screen

in sheet mold during the paper forming operation is passed down the drain.

B. Fourdrinier Paper Machine

The laboratory Fourdrinier is designed to simulate a commercial papermaking process. Its operating speed is 2 feet to 8 feet per minute and it produces a 9-inch-width sheet. Speed in this study was 5 fpm. Major components are:

1. Headbox - The headbox is a constant volume tank located at the foot of the Fourdrinier wire. It is shown in the upper left-hand corner of Figure 9. At the headbox, the incoming fiber-pigment suspension from the Fourdrinier mixing tank (Figure 11) is blended with recirculated white water. The white water is used as dilution water. The feed pump of the Fourdrinier (Figure 10) is a Sigamotor Finger Pump driven by a variable speed drive.

2. Fourdrinier Section or Wet End (Figure 9) - This section consists of the wire, suction boxes and suction roll. Pictured in Figure 9 from left to right are the headbox, wire, suction boxes and suction roll. The pulp-pigment suspension is passed from the headbox through a slice to the endless Fourdrinier wire during sheet formation. As the sheet progresses down the wire, it continuously loses water, initially by gravity and then by suction, when it reaches the suction boxes and suction rolls. The water containing pigment and fiber which is not retained on the wire is collected in a tray beneath the wire and pumped (Figure 11) back to the headbox where it is blended with the incoming pulp-pigment suspension. Overflow water from the headbox and water pulled through the suction boxes and suction roll is not reused.

3. Press Section - Directly after the suction roll is the press section, shown in Figure 6, which consists of one first pass, one second reversing press and one smoothing press with bottom rolls. At the press section, water is removed from the unsupported sheet by passing the sheet through a series of rolls under pressure. The water is absorbed by a series of felts.

4. Dryer Section - The dryer section, pictured in the right of Figure 8, consists of 14 paper dryers made of cast bronze, electrically heated and arranged in three groups of 2 x 4 and 6 dryers.

5. Reel - The reel shown in the lower right of Figure 8 is a roll for collecting paper.

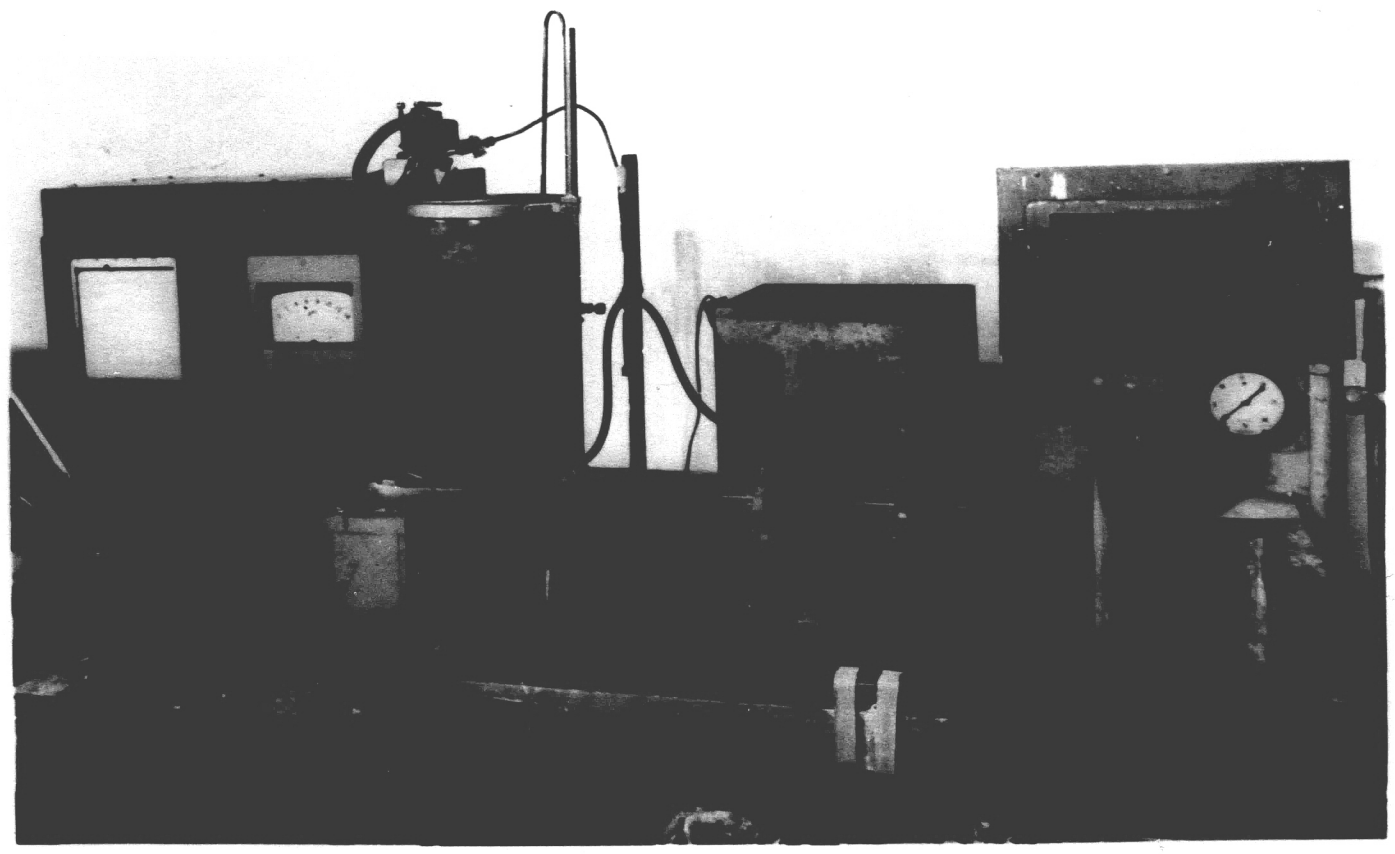


Figure 4

Noble and Wood Handsheet Machine
Left to Right: pH Recorder
Proportioner
Sheet Mold
Control Panel

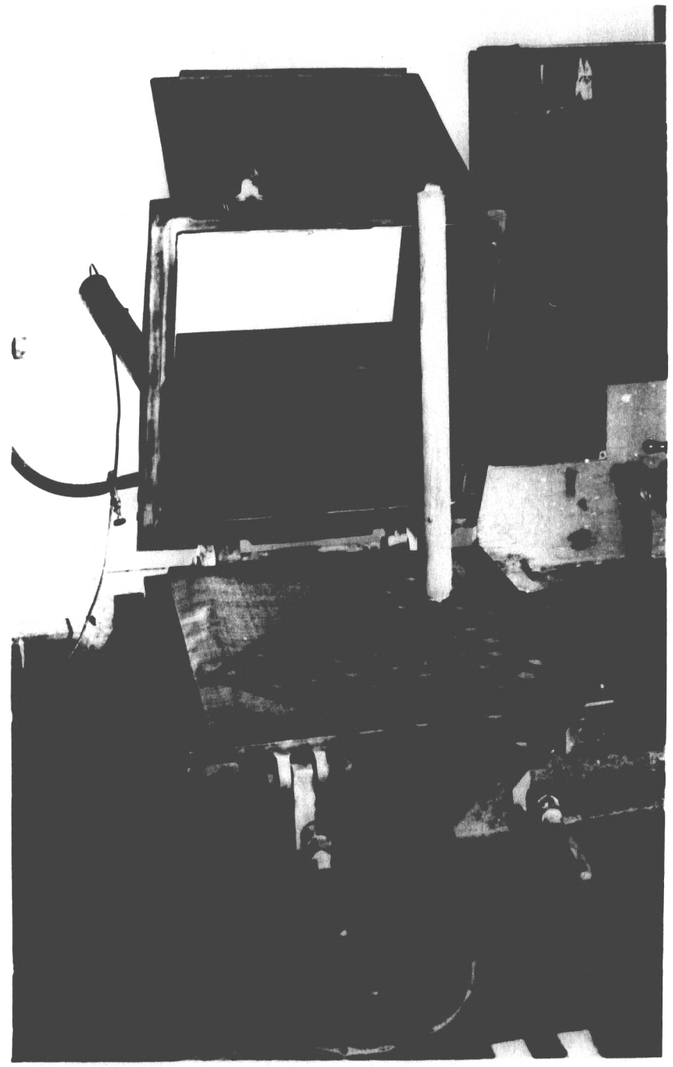


Figure 5

Noble and Wood Handsheet Machine
Sheet Mold

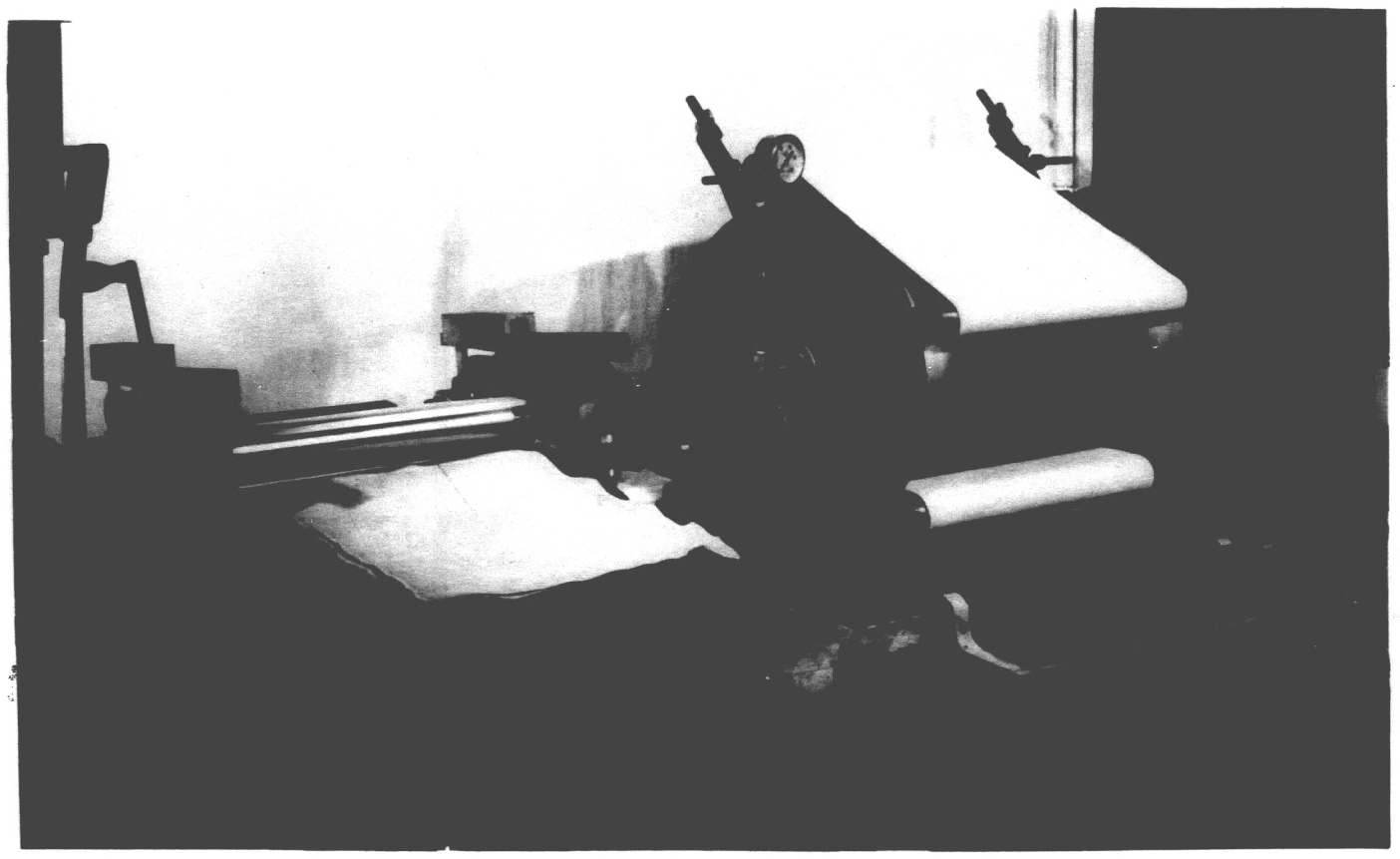


Figure 6

Noble and Wood Handsheet Machine
Left to Right: Press
Dryer

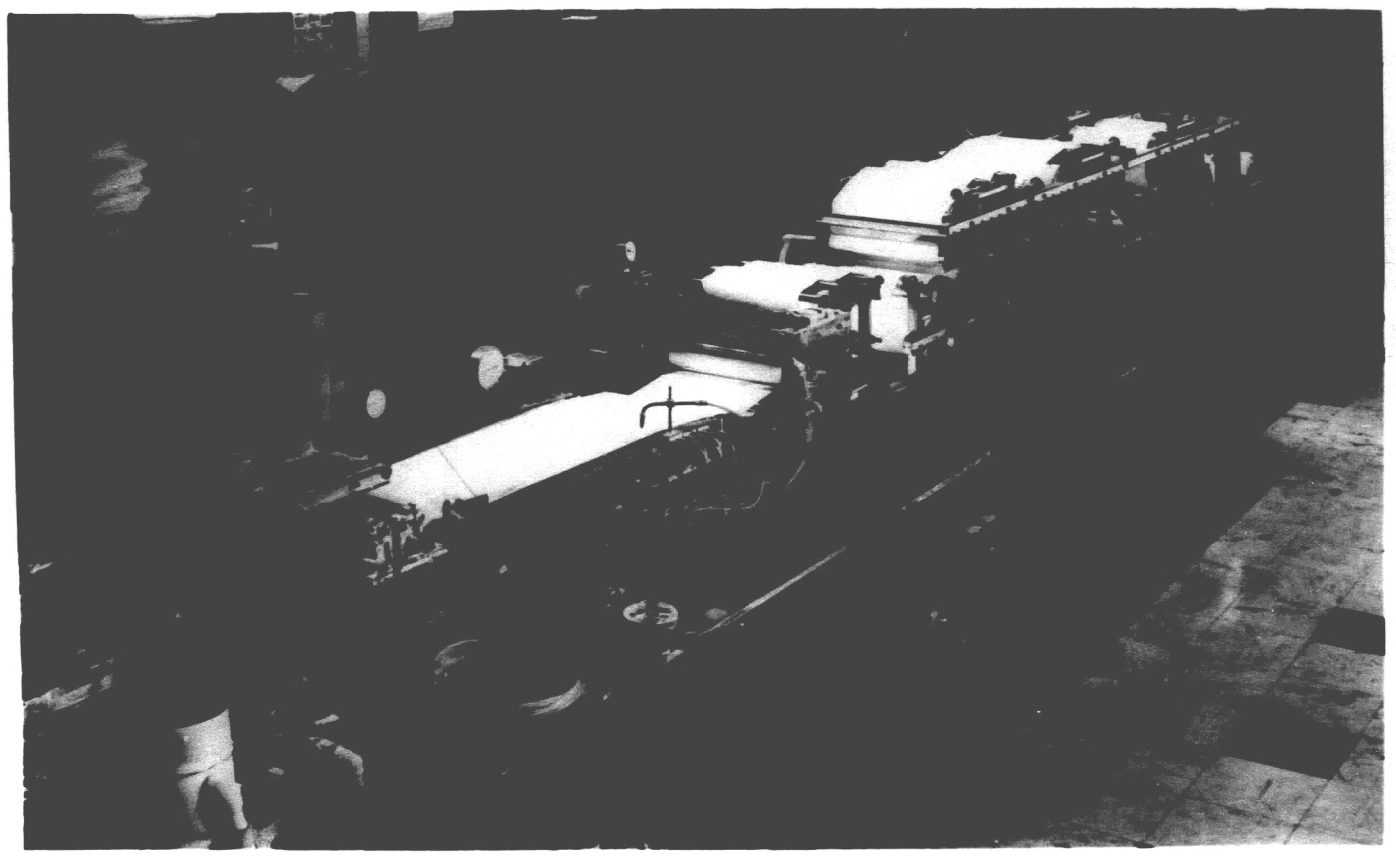


Figure 7

Fourdrinier Paper Machine
View from Wet End

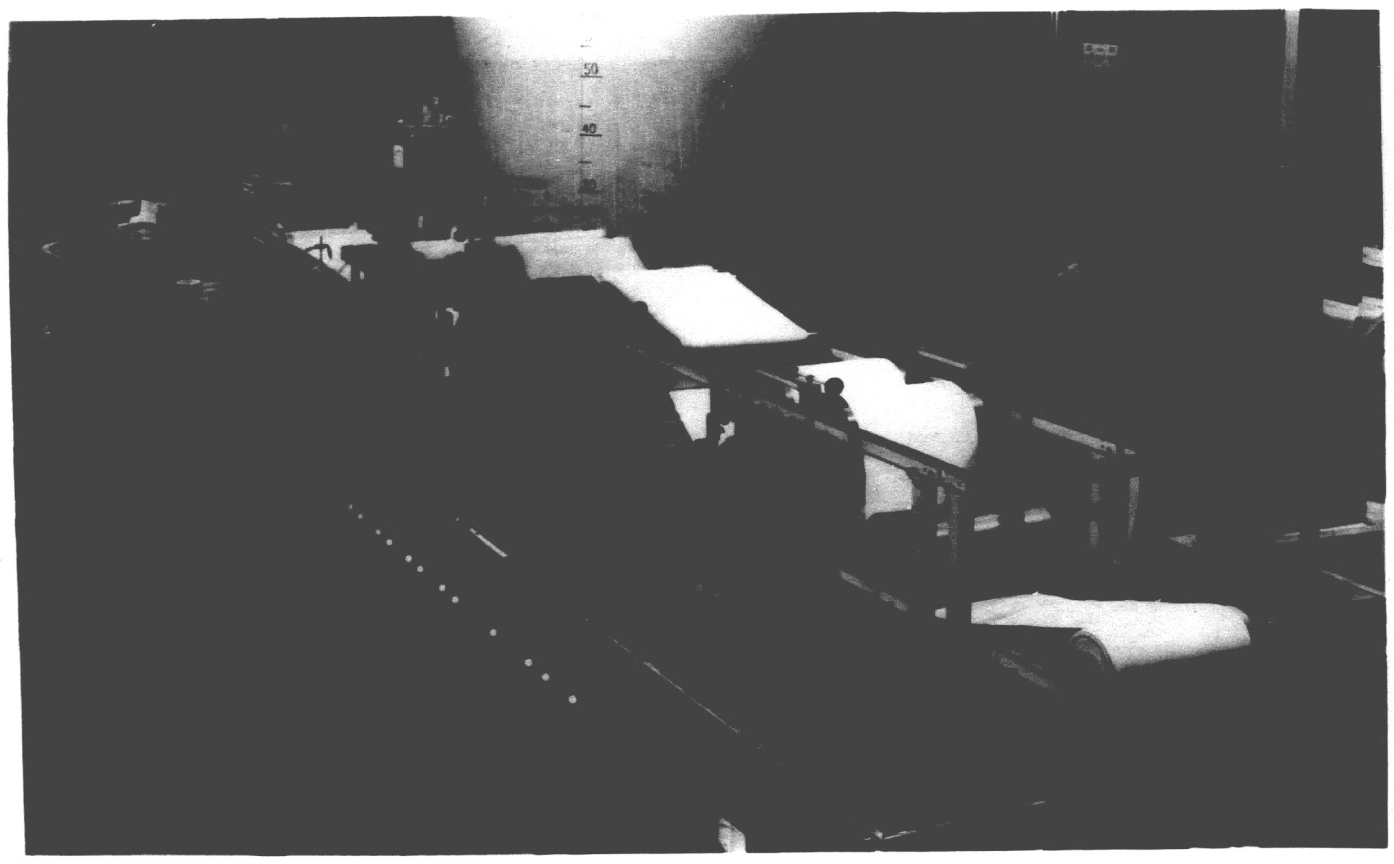


Figure 8

Fourdrinier Paper Machine
View from Dryer Section

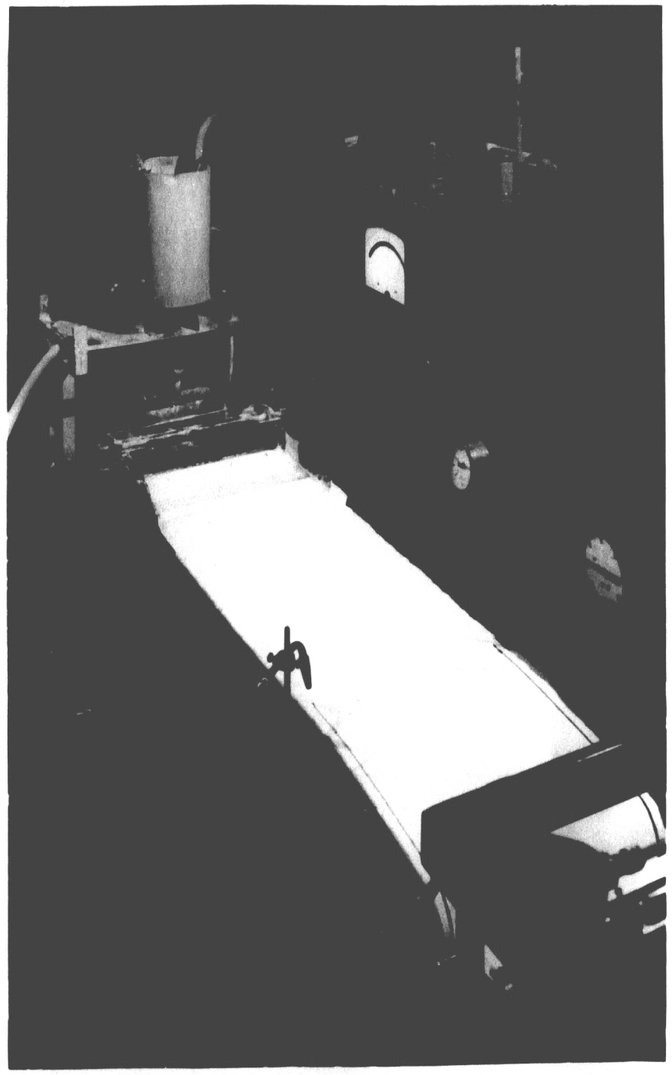


Figure 9

Wet End of Fourdrinier

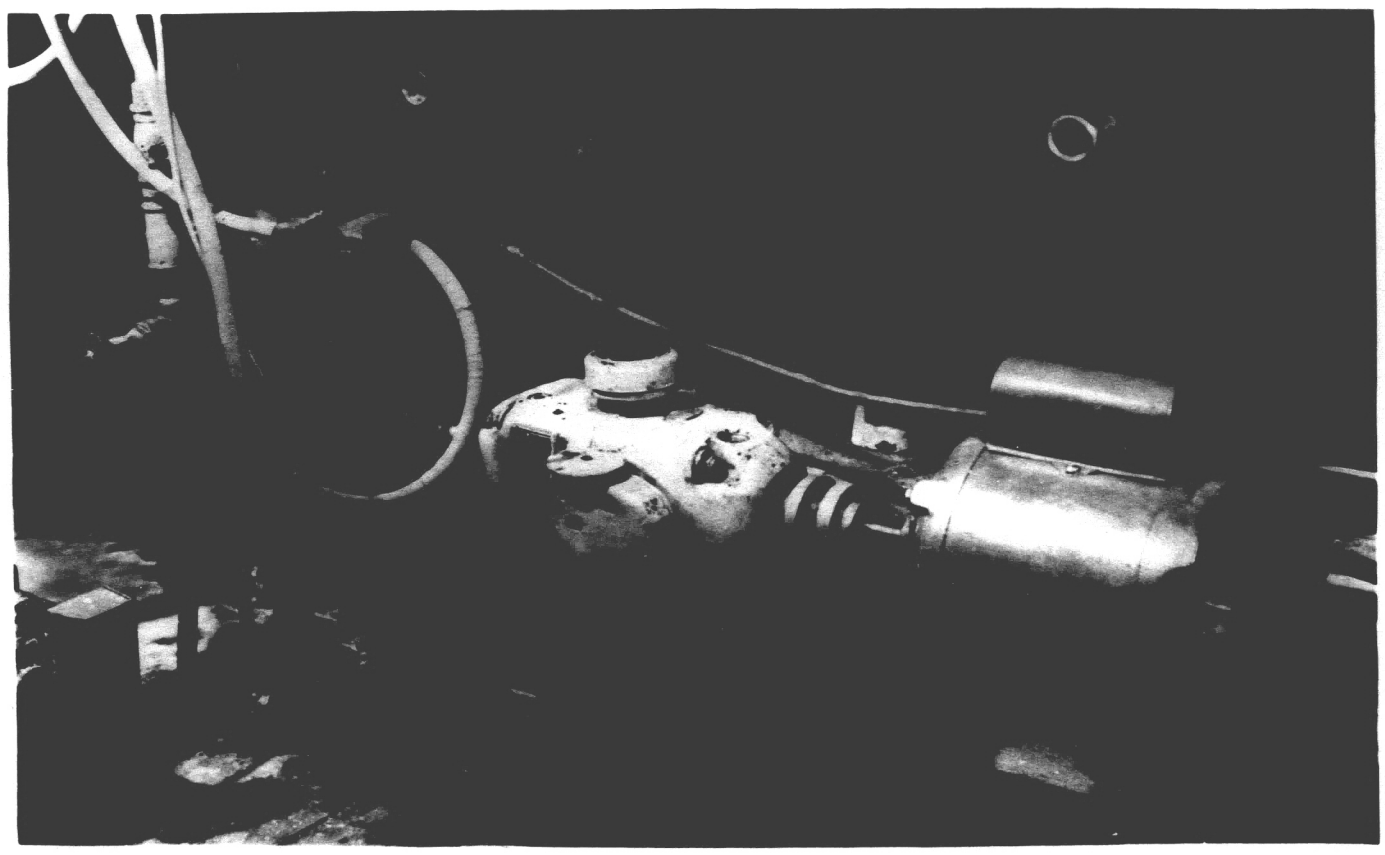


Figure 10

Feed Pump of Fourdrinier

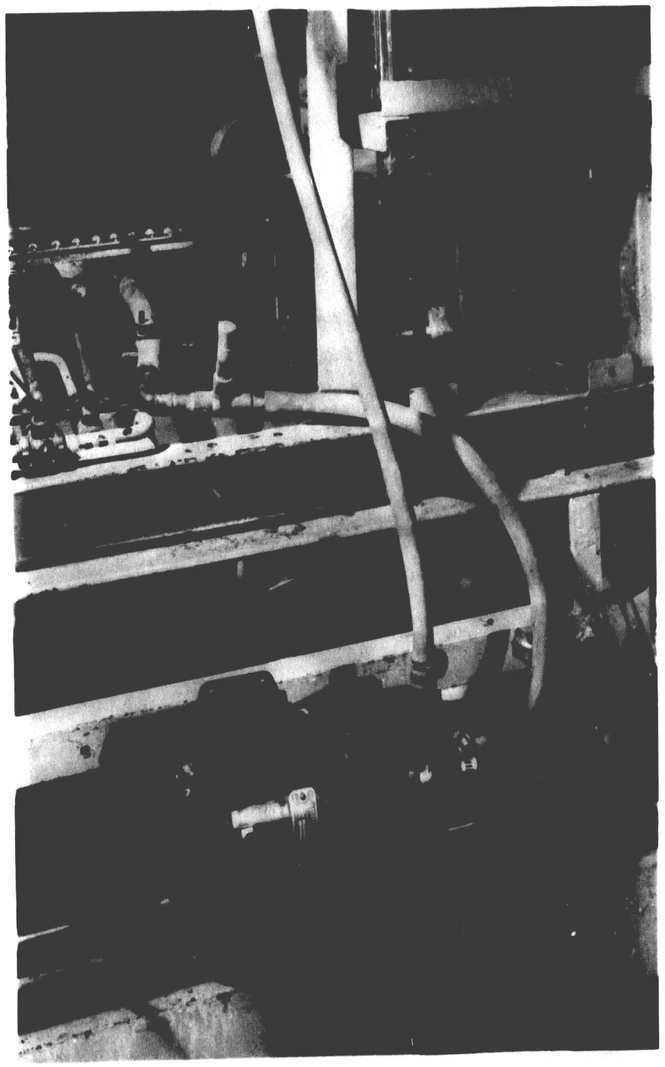


Figure 11

Recirculating White Water Pump
of Fourdrinier

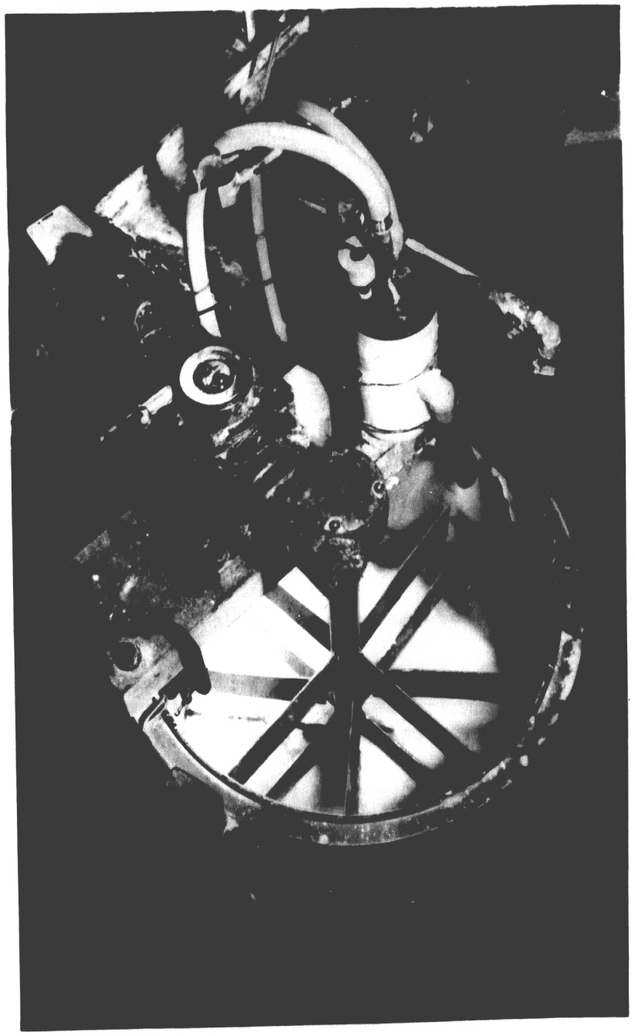


Figure 12

Stock Chest of Fourdrinier

IV. Test Procedure

A. Phase I

The initial phase of the program was conducted on the Noble and Wood Handsheet Machine studying the following combinations of variables:

Variable	Level
Alum	1% and 2% based on weight of pulp
Rosin	0% and 1% based on weight of pulp
Pigment	10.6% based on weight of pulp
Water	Raw and demineralized
pH of Pigment - Fiber Suspension	4.5, 5.5 and 6.5
Order of Addition of Additives	(a) Size, alum, pigment (b) Pigment, size, alum (c) Alum, pigment, size

Due to the limitations in pulp preparation and storage facilities, it was necessary to conduct this experiment in four stages. Order of testing was randomized wherever possible to eliminate possible bias on results caused by variations in the conductivity of demineralized water and pulp freeness. A block diagram of experiment is shown in the Appendix (Table A-I).

1. Preparation of Pulp Masterbatch - One thousand seven hundred fifty grams of Puget Sound bleached sulfite pulp with 80 l. of water were beaten to 540 ml. Schopper Riegler freeness in a 5-pound Valley beater. The Schopper Riegler Freeness Tester is a standard method of measuring pulp freeness during beating. Initially, the pulp was beaten 15 minutes without load. After this interval, a load of 23 pounds was applied to the lever arm of the bedplate. Beating was continued until a freeness of 540 ml. was reached. Two freeness determinations were made when the 540 ml. level was reached; agreement between successive determinations was held to $\pm$10 ml. After beating was completed, the pulp was divided into aliquot parts, each containing 28.3 gm. of ovendry fiber. Thirty-six different papermaking conditions were run with each batch of pulp.

2. Preparation of Demineralized Water Masterbatch - Raw well water was passed through a two-column Barnstead demineralizer. The water leaving this demineralizer had a specific resistance of 100,000 ohms-cm. and a pH between 7.0 and 9.0. The treated water was stored in a 1,500-gallon, rubber-lined tank.

3. Papermaking Process - The pigments were incorporated in paper made on the 12 inch by 12 inch Noble and Wood Handsheet Machine described earlier.

   a. Addition of Additives - Alum, pigment, and size were added to the pulp suspension using a Tappi Pulp Standard Disintegrator. The disintegrator is a high speed mixer inside of a baffled mixing vessel. The following mixing schedule was used: First material was added to the pulp suspension and mixed for one minute. The second material was then added and the resulting suspension was mixed for one additional minute. The final material was added and the entire suspension was mixed for three minutes.

   After mixing, the suspension was poured into the proportioning tank of the Noble and Wood Handsheet Machine where it was diluted with water to provide a suspension containing 2.06 gm. of overdry fiber per liter of suspension.

   b. Formation of Handsheets - A 1.89 l. volume of the pigmented pulp suspension was drawn from the proportioning tank and poured into the Noble and Wood sheet mold which was partially filled with water. The suspension was further diluted at the sheet mold with approximately 21 l. of water.

   At the mold, the required volume of H_2SO_4 or NaOH was added to bring suspension to desired pH. The drop valve on the sheet mold was then opened, allowing the water and unretained pigment to drain away from the fiber, which was deposited on the screen of the sheet mold.

   The wet sheet and supporting screen were then pressed. The combination of press weights and felt conditions were such that they yielded a wet mat of 32 percent consistency (percent dry solids).

After pressing, the sheet and screen were passed through a rotary dryer which was maintained at a temperature of 190°F.-200°F. Drying time was three minutes.

The various steps used to form each handsheet were repeated five times to make five handsheets from each batch of pigmented pulp.

4. Calendering - Before calendering, the sheets were conditioned at 50 percent relative humidity and 77°F. for 18 hours. The calender was run for 30 minutes prior to calendering of any sheets.

   Each sheet was calendered with 10 passes through a cotton steel nip with a loading of 1,666 pounds per lineal inch.

5. Analysis and Testing of Handsheets - After calendering the handsheets were tested to determine opacity, brightness, and basis weight. A spherical reflectometer was used for opacity and brightness determinations.

   Titanium dioxide content of the paper was determined using the Autrometer. The Autrometer, manufactured by the Phillips Electronic Instrument Company, Mount Vernon, New York, is a comparative X-ray fluorescence spectrometer which compares the intensity of a secondary X-ray at a particular wavelength of the material being analyzed with a titanium metal reference standard. Chemical analysis was used to establish a calibration curve for this instrument.

B. Phase II

This phase of the program was conducted both on the handsheet and the Fourdrinier.

The reaction vessel in the handsheet test consisted of a 55-gallon plastic line drum and a Rockwell Compactool Drill Press, used as an agitator. The stirring rod on the drill press had a 32-inch shaft and three 2-1/2 inch stirring blades. The agitator shaft was at a slight pitch in the drum during agitation. The

photograph (Figure 13) shows this vessel. While under agitation, the pH of the pulp-pigment suspension was monitored by a Leeds and Northrup Model 7401 pH meter and recorder. This instrument is shown in Figure 4.

The handsheet program of this phase of the experiment showing the variables studied is outlined in Table II.

Table II

Experimental Conditions of Phase II Handsheet Program

Run No.	Type Water	% Alum Based on Fiber	% Rosin Based on Fiber
600-10	Well	0	0
600-9	Well	1	0.5
600-2	Well	2	1
600-4	Well	4	2
600-5	Demineralized	0	0
600-8	Demineralized	1	0.5
600-7	Demineralized	2	1
600-6	Demineralized	4	2

In all cases, one batch containing 1750 gm. of bleached sulfite pulp and 80 l. of water beaten to a 540 ml. Schopper Riegler freeness was initially added to the reaction vessel (Figure 13). TiO_2 (11.1 percent on weight of pulp) was added to the pulp and mixed for 20 minutes. Next, rosin size solution, concentration 32.4 gm. per l., was added and mixed for 20 minutes. Alum solution, concentration 66.6 gm. per l., was then added. As soon as the required amount of alum was added, total pulp-pigment suspension samples were taken at selected time intervals. The suspensions were placed in the proportioning tank of the handsheet machine and five 30-pounds-per-ream handsheets were made with each

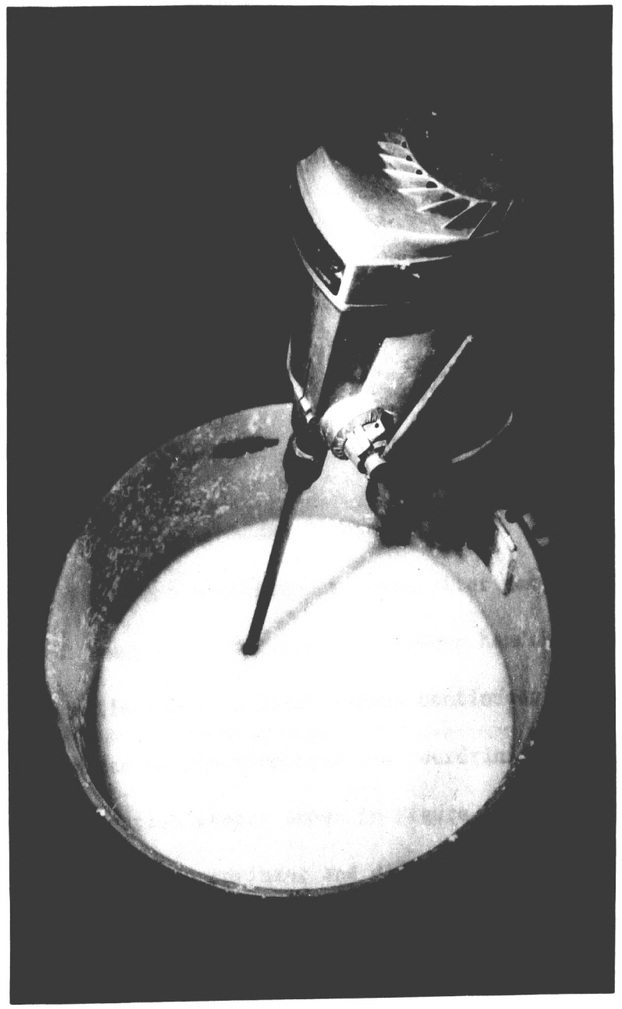


Figure 13

Reaction Vessel Used in Handsheet Program

suspension. The paper samples were tested for TiO_2 content, opacity, brightness and basis weight as outlined earlier.

The Fourdrinier program of this phase is outlined below. Demineralized water was used in all test runs.

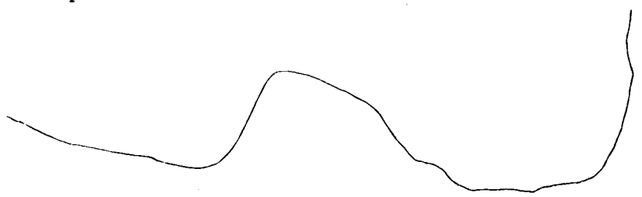
Table III

Experimental Conditions of Phase II Fourdrinier Program

Run No.	% Alum on Fiber	% Rosin Size on Fiber	Recirculation
600-11	4	2	No
600-12	4	2	Yes
600-13	2	1	No
600-14	2	1	Yes
600-15	0	0	Yes
600-16	2*	1	Yes
600-17	2**	1	Yes

*Alum added in white water recirculating line
**Alum and rosin size added in beater

Test runs were made without white water recirculation for the purposes of judging the differences between handsheet and Fourdrinier due to differences in batch versus continuous operation. One major difference in the handsheet and Fourdrinier program was the Fourdrinier reaction vessel shown in Figure 13. This tank is the mixing tank of the Fourdrinier and differs from the handsheet reaction vessel in volume, type agitator, speed of agitation and in that it contained baffles. Pigment, alum and rosin size were added to the pulp suspension using the same schedule as handsheet work. Paper samples were tested in similar manner.



ANALYSIS OF EXPERIMENTAL DATA

I. Phase I

The properties of major concern in this investigation were optical efficiency and pigment retention.

The Kubelka-Munk Theory was used to determine the optical efficiency of TiO_2 in the various papermaking systems. Scattering coefficients of TiO_2 (Spig) in the various systems were calculated using the following relationship:

$$\frac{(S_x)}{(BW)\ Paper} = (S)\ Pulp\ \frac{(\%\ Pulp)}{100} + (S)\ Pigment\ \frac{(\%\ Pig.)}{100} \qquad (7)$$

S_x - Scattering power of paper determined from opacity and brightness determinations.

(S) Pulp - Scattering coefficient of pulp determined from optical data on unpigmented paper.

BW Paper - Basis weight of paper.

(S) Pig. - Scattering coefficient of pigment in particular system. Basis for optical efficiency comparisons.

Equation 7 was shown as above to emphasize additive effect of the scattering efficiency of the various components of the sheet on the overall scattering power of the sheet.

Retention was calculated from:

$$\%\ Pigment\ Retention = \frac{\%\ Pigment\ in\ Sheet}{\%\ Pigment\ Added} \times 100 \qquad (8)$$

A summary of the data is given in the Appendix (Table A-II to A-V).

After calculating the scattering coefficients and pigment retention, an analysis of variance calculation was made to determine the sources and magnitudes of the errors present and to assess the significance of differences between the various systems.

A. Analysis of Variance

Variance can be defined as the sum of the squares of the deviations of the observations from their mean divided by one less than the total number of observations. A property of variance is that when an experiment has a number of factors each making a contribution to the variance of the final result then this variance is equal to the sum of the component variances. This property of additiveness of variance makes possible the analysis of variance technique used in this experiment. The total variance of the experiment was analyzed into its component variables. The relative importance of the variables was found by using the F statistic which is described, simply, as a variance ratio. The variance associated with each variable divided by the residual variance of the experiment yields an F value. By comparing the calculated value with standard F values at various confidence or probability levels, the importance of the individual variables and interactions on the final result was determined. Further information including "F" statistic values is found in Brownlee[16].

In a table of data, there is a variance (mean square) associated with each term. The variance is the variability that will occur if all other terms are held constant. For example, the mean square associated with A (alum) is the variability if O, H, S and W are held constant. The interactions are a measure of the effect of one variable on the other: example, AH is a measure of the extent the A effect depends on the value of H, and, conversely, to which the H effect depends on A - similarly for the other interactions.

The error estimate is that portion of the variability which cannot be allocated to the controlled variables.

Degrees of freedom can be defined as the number of observations minus the number of constraints in an experiment.

B. Scattering Coefficient (Optical Efficiency)

The analysis of variance for the scattering coefficients is given in Table A-VI in the Appendix. Results in this table are based on scattering coefficients multiplied by 100 which was done to simplify calculations. All interactions third order and above, smaller than the residual, were included in the error estimate. Final estimate was mean square of 4.519 with 24 degrees of freedom corresponding to a standard deviation of 0.0146 of a single scattering coefficient.

In the following discussion, the symbols defined below are used:

A denotes alum
RW denotes raw water
DW denotes demineralized water
S denotes size
H denotes pH
O denotes order of addition
F denotes "F" statistic
DF denotes degrees of freedom

To test whether individual variables or interactions had a significant effect on optical efficiency, the F statistic, as noted earlier, was used. For present experiment, "F" statistic values are shown in Table IV.

Table IV

"F" Statistic Values of Phase I Scattering Coefficient Results

	80%	95%	99%
F (DF 1,24)	1.7	4.3	7.8
F (DF 2,24)	1.7	3.4	5.6
F (DF 4,24)	1.6	2.8	4.2

Source of Scattering Coefficient Variation	F Ratio	Level of Significance
A	153.4	99
AH	3.4	95
S	225.4	99
AS	23.2	99
AHS	4.6	95
W	377.4	99
AW	368.8	99
SW	145.3	99
ASW	159.5	99
O	47.3	99
AO	8.2	99
AHO	2.30	80
SO	33.9	99
ASO	12.4	99
AWO	11.4	99
SWO	5.1	95
ASWO	6.7	99

The effect of alum, rosin size, order and water on scattering coefficient holding all other variables constant are shown in Table V.

Table V

Effect of Individual Variables on Phase I
Scattering Coefficient Results

A. Alum		1%	2%	
Scattering Coefficient	$\sigma = 0.0024$	0.817	0.755	
B. Rosin Size		0%	1%	
Scattering Coefficient	$\sigma = 0.0024$	0.748	0.823	
C. Water		Raw	Demineralized	
Scattering Coefficient	$\sigma = 0.0024$	0.834	0.737	
D. Order		A	B	C
Scattering Coefficient	$\sigma = 0.0028$	0.819	0.761	0.777

Table V shows that an increase in alum concentration and demineralized water has a negative effect while rosin size has a positive effect on optical efficiency. Order A, i.e., size, alum and pigment yields best efficiency. Further discussion will be given later.

While the above analysis gives the effect of individual variables, results are meaningless when taken alone because as shown in the analysis of variance table there are several interactions which are highly significant. Second order interactions are shown in Table VI. The alum water interaction shows a 20 percent optical efficiency difference at the 1 percent alum level with raw water yielding higher efficiency than demineralized water.

Table VI

Alum-Water Interaction Phase I
Scattering Coefficient

	1% Alum	2% Alum	
Raw Water (RW)	0.914	0.755	$\sigma = 0.0034$
Demineralized Water (DW)	0.720	0.754	

The most significant third order interaction alum, size and water yields optimum efficiency in the 1 percent alum, 0 size and raw water system.

Table VII

Alum-Water-Size Interaction Phase I
Scattering Coefficient

		RW	DW	
1% Alum	0% Size	0.950	0.633	
	1% Size	0.877	0.807	σ = 0.0048
2% Alum	0% Size	0.704	0.706	
	1% Size	0.813	0.802	

The fourth order interaction alum, size, water and order was significant at the 99 percent level. Results are shown in Table VIII.

Table VIII

Alum-Water-Size-Order-of-Addition Interaction
Phase I Scattering Coefficient

		Order A		Order B		Order C		
		RW	DW	RW	DW	RW	DW	
1% Alum	0% Size	0.945	0.665	0.929	0.550	0.975	0.683	
	1% Size	0.916	0.817	0.890	0.819	0.825	0.786	σ = 0.0084
2% Alum	0% Size	0.794	0.749	0.640	0.663	0.678	0.703	
	1% Size	0.834	0.825	0.776	0.823	0.807	0.759	

Optimum overall efficiency results are in the 0 size, 1 percent alum, raw water order C, system.

C. Pigment Retention

A complete analysis of variance tabulation is given in Table A-VII. Pooling of mean squares in similar fashion as done with scattering coefficients yields a new residual mean square of 2.986 with 38 degrees of freedom and the standard deviation of a

single pigment retention determination of 0.48. F values for retention values are shown in Table IX.

Table IX

"F" Statistic Values - Retention Results of Phase I

	80%	95%	99%
F (DF 1,38)	1.7	4.1	7.4
F (DF 2,38)	1.7	3.2	5.2
F (DF 4,38)	1.6	2.6	3.8

Source of Variation	F Ratio	Level of Significance
A	60.6	99
AH	17.8	99
S	36.2	99
W	682.1	99
HS	1.8	80
AHS	1.8	80
AHW	5.7	99
ASW	9.1	99
O	95.7	99
AO	5.4	99
HO	1.6	80
SO	2.0	80
WO	1.9	80
AWO	4.5	95
SWO	8.0	99

Tabulated below are the effects of variations in the individual variables on TiO_2 retention.

Table X

Effecting of Individual Variables
on Retention Results of Phase I

A. Alum		1%	2%
% Retention	$\sigma = 0.49$	32.09	35.26
B. Rosin Size		0%	1%
% Retention	$\sigma = 0.49$	40.78	34.90
C. Water		RW	DW
% Retention	$\sigma = 0.49$	28.36	39.00
D. Order		A	B C
% Retention	$\sigma = 0.62$	34.9	29.7 36.3

Recalling the scattering coefficient results, it is seen that with the exception of order of addition the more favorable retention results are obtained at variable levels other than levels in which most favorable efficiency results were obtained. As noted earlier, this inverse relation between retention and optical efficiency is one of the major problems in pigment use in the paper industry. A method for combining these properties is developed later.

The most significant of the third order interactions was the alum, size, water response.

Table XI

Alum-Size-Water Interaction
Phase I Retention

		RW	DW	
0% Size	1% Alum	24.95	36.65	
	2% Alum	29.25	38.96	$\sigma = 0.98$
1% Size	1% Alum	28.83	37.94	
	2% Alum	30.41	42.44	

As expected the optimum retention yielding systems did not yield the highest optical efficiency.

D. Combining Retention and Scattering Coefficient

The properties of retention and scattering coefficient for the alum-size-water interaction were combined to determine the percent TiO_2 which must be added to the system to give a sheet having a scattering power of 1.5.

A sample of calculation follows:

System 1% Alum 0 Size Raw Water

S_x paper = 1.5
BW paper = 30.0
S pulp = 0.0289
S pigment = 0.950
% Retention = 24.95

Substituting in Equation 7:

$$\frac{1.5}{30} = 0.0289 \left(\frac{100 - \% \text{ Pig.}}{100}\right) + \left(\frac{\% \text{ Pigment}}{100}\right) (0.950)$$

$$\% \text{ Pigment} = 2.25\%$$

This is the amount of pigment required in the sheet. Therefore, the amount of pigment that must be added to the system after adjusting for retention will be 2.25/0.2495 or 8.49 percent. Summarized in Table XII are results of similar calculations for remaining systems.

Table XII

Alum-Size-Water Interaction
Phase I Pigment to be Added

		RW	DW
1% Alum	0% Size	8.49	9.81
	1% Size	8.64	7.35
2% Alum	0% Size	10.70	8.23
	1% Size	8.86	6.62

Since the lowest pigment requirement is best, it can be concluded that the optimum system for TiO_2 is the 1 percent size, 2 percent alum, demineralized water system.

Later, in Phase II Runs FR-600-5-8, optimum pigment addition results are also found in the 2 alum:1 rosin system.

II. Phase II

On the basis of the results of Phase I in which the variables of alum concentration, rosin size concentration and type water were found to have the most significant effects on the properties of retention and optical efficiency, these variables and the effect of reaction time were studied in Phase II. Reaction time was emphasized because the major objective of this phase of the program was to determine the differences in TiO_2 retention and optical efficiency between the Fourdrinier and handsheet machine. An additional variable, the effect of variation in location of additive feed on the Fourdrinier, was also studied in the final stage of this program. A summary of the handsheet data of this phase is given in Tables A-VIII to A-XV in the Appendix.

The handsheet operation of Phase II differed from the handsheet operation of Phase I chiefly in the reaction time of pulp-pigment, alum and rosin size. In Phase I, the time was constant at 5 minutes while in Phase II reaction time was varied from 15 seconds to 6 hours.

Retention and scattering coefficient were initially plotted versus time for each run. The curves which are shown in Figures 14-17 are based on a polynomial regression using an IBM 1130 computer. In all cases, curve fitting was done for ease of analysis and should not be regarded as a final correlation. Multiple regression analysis on all handsheet data was conducted using both scattering coefficient and retention as dependent variable and time of reaction, pH of reaction, type water, alum concentration,

rosin concentration and various interactions as independent variables.

The response of retention and scattering coefficient to reaction time were assumed to be of the form:

$$R = A + Bt + Ct^2 + Dt^3 + Et^4 \quad (9)$$

$$S = A_1 + B_1t + C_1t^2 + D_1t^3 + E_1t^4 \quad (10)$$

Where:

R = Retention
S = Scattering Coefficient
t = Time in minutes
A, B etc. = Regression Coefficients

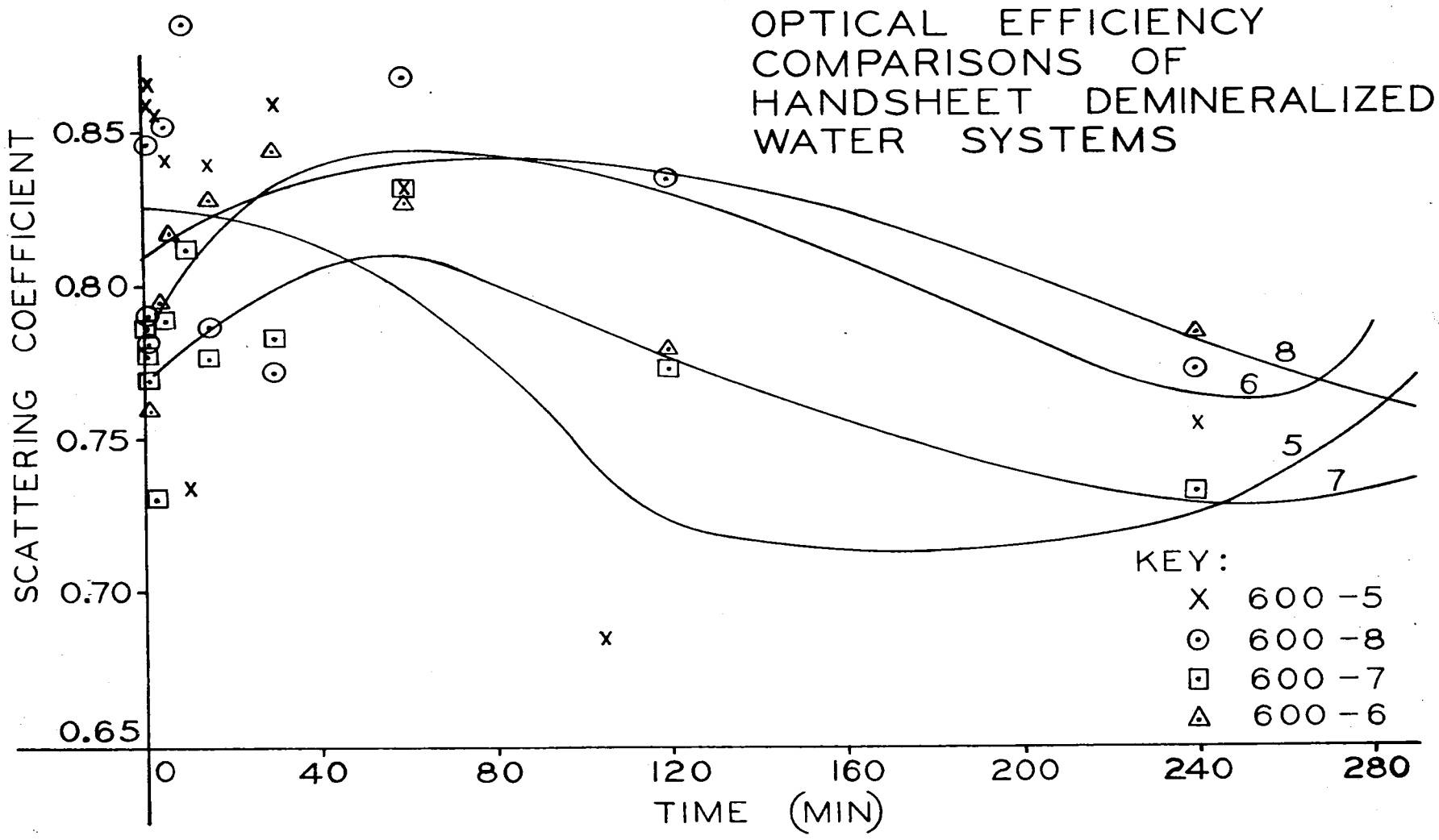
The above equations were obtained using a standard polynomial regression analysis.

A. Scattering Coefficient (Handsheet Test Runs)

Regression equations for the individual runs are given in Table A-XVI. Curves of these equations are shown in Figures 14 and 15. Steady state is not attained after 6 hours with respect to scattering coefficient. The trend was toward an increase in scattering coefficient with increasing alum and rosin concentration. Table V, Phase I scattering coefficient results, shows a decrease in this property on increasing alum from 1 percent to 2 percent and an increase on the addition of rosin size.

The demineralized water systems differed from the raw water systems. The trend was toward increasing scattering coefficient in the 4- to 6-hour time period for the demineralized water systems and there was no general dependency of coefficient on alum and rosin level.

FIGURE 14
OPTICAL EFFICIENCY
COMPARISONS OF
HANDSHEET DEMINERALIZED
WATER SYSTEMS



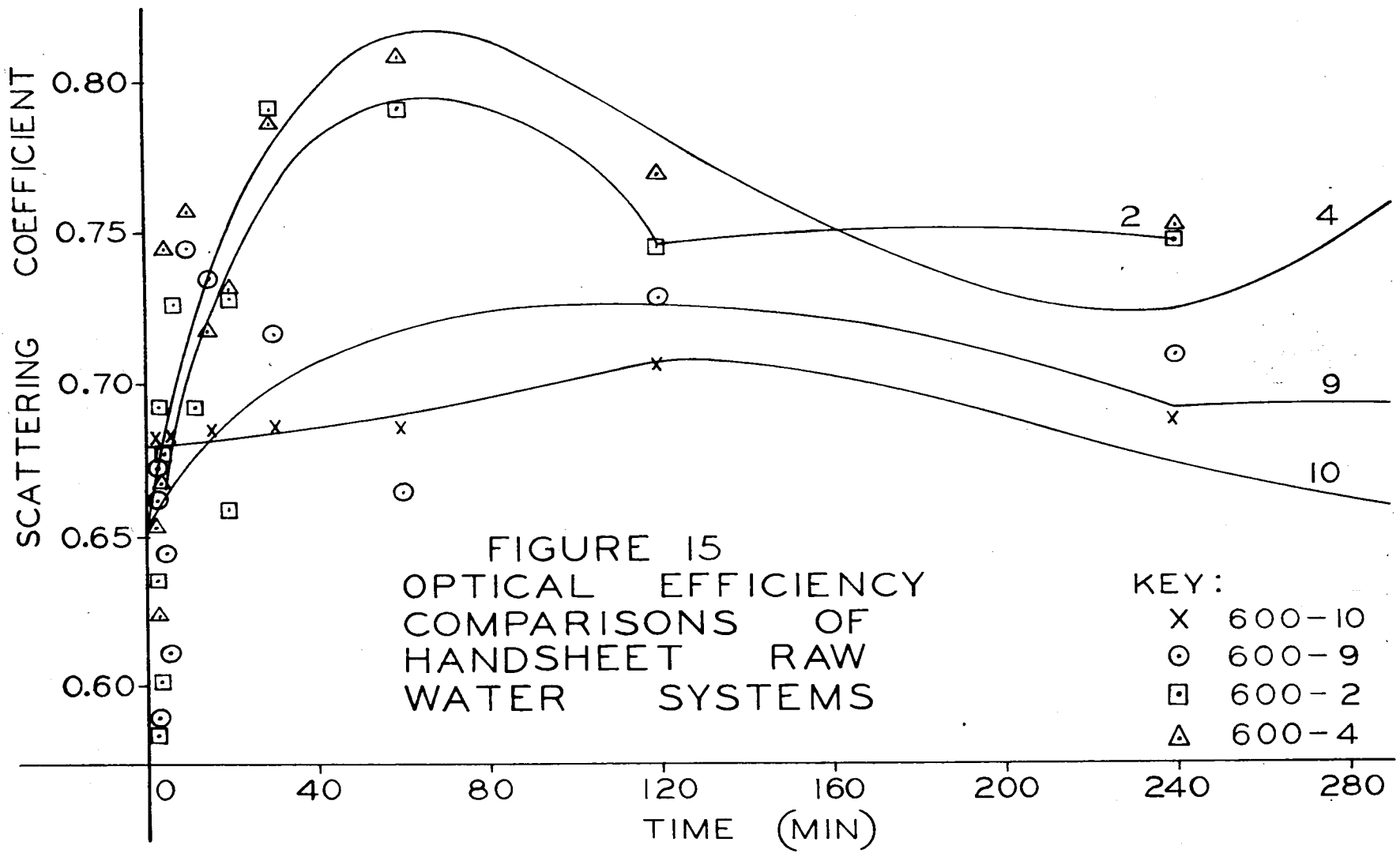


FIGURE 15
OPTICAL EFFICIENCY
COMPARISONS OF
HANDSHEET RAW
WATER SYSTEMS

At equal rosin and alum levels, the TiO_2 used in demineralized water was more efficient optically than in raw water. Opposite results were obtained in Phase I.

B. Retention (Handsheet Test Runs)

The relationship between retention and time are summarized in the regression equations given in Table A-XVII in the Appendix. Figures 16 and 17, the curves of these equations, show increasing retention with increasing time, alum and rosin size. Sharpest increase occurs in the initial 2 hours.

Retention comparisons in raw and demineralized water are illustrated in Figures 18, 19 and 20 and show an advantage for demineralized water in all cases. However, with no alum or rosin in a system, TiO_2 in raw water shows higher retention than in demineralized water. The cations, Ca^{++}, Mg^{++}, in the raw water flocculate the TiO_2 which is reason for higher retention.

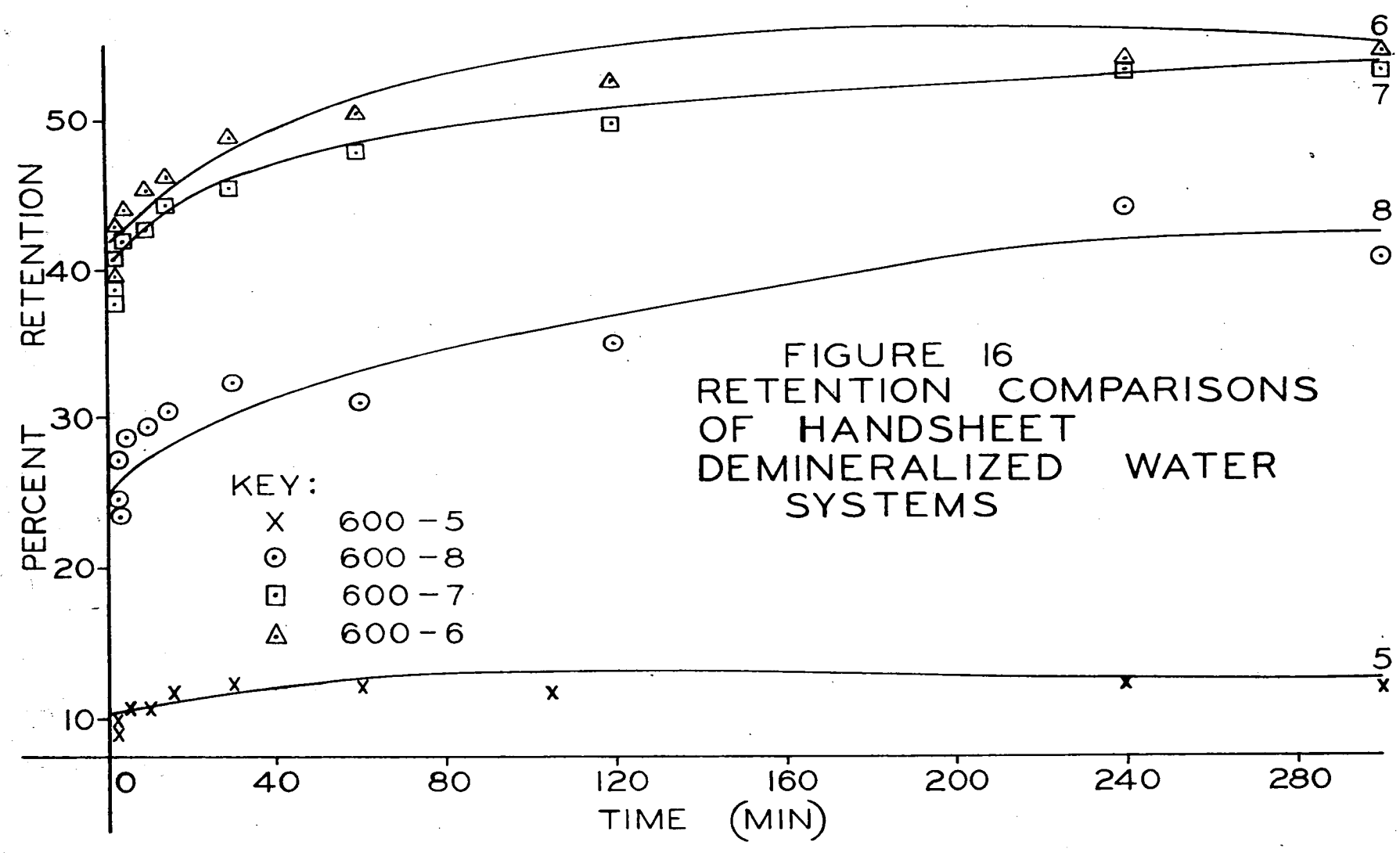
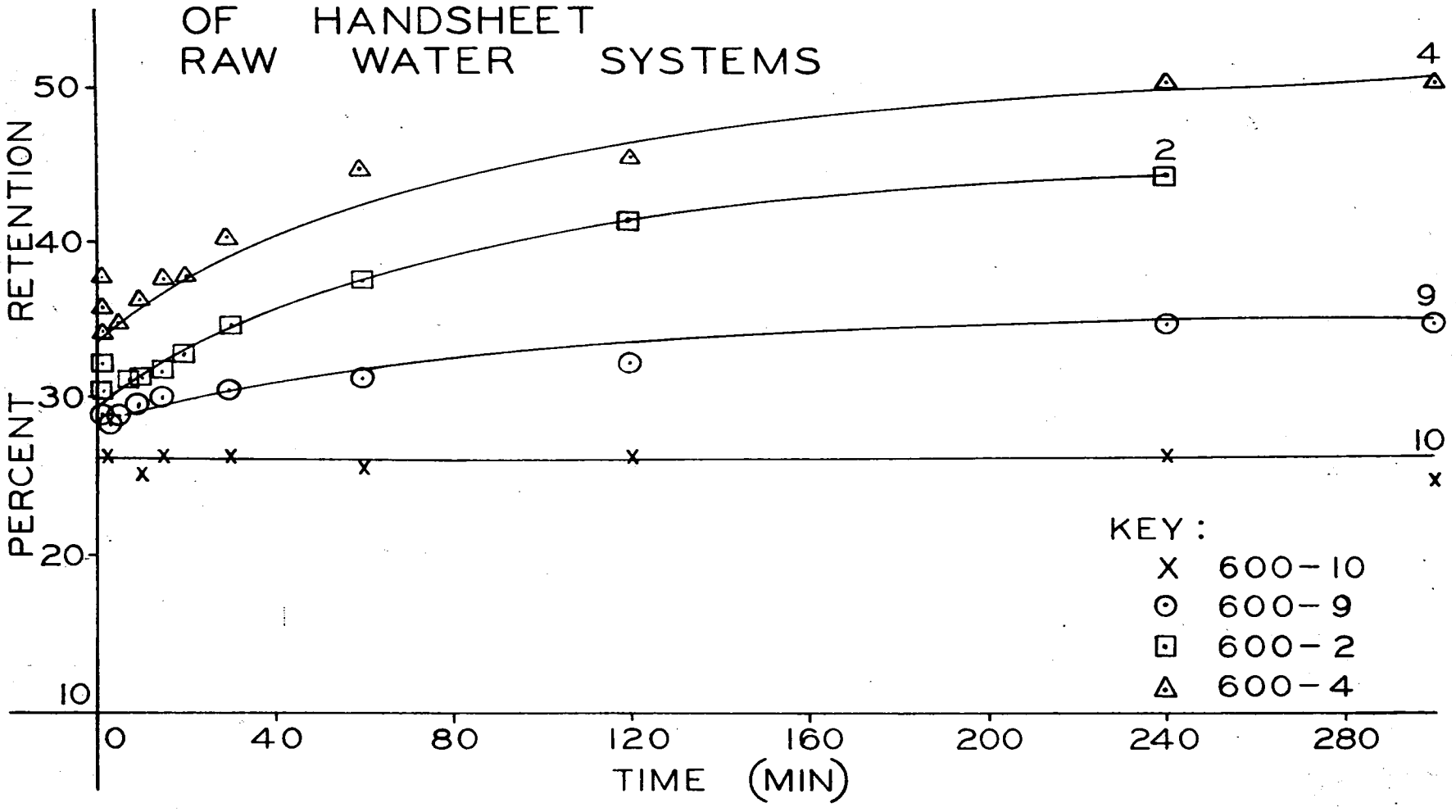


FIGURE 16
RETENTION COMPARISONS
OF HANDSHEET
DEMINERALIZED WATER
SYSTEMS

FIGURE 17
RETENTION COMPARISONS
OF HANDSHEET
RAW WATER SYSTEMS



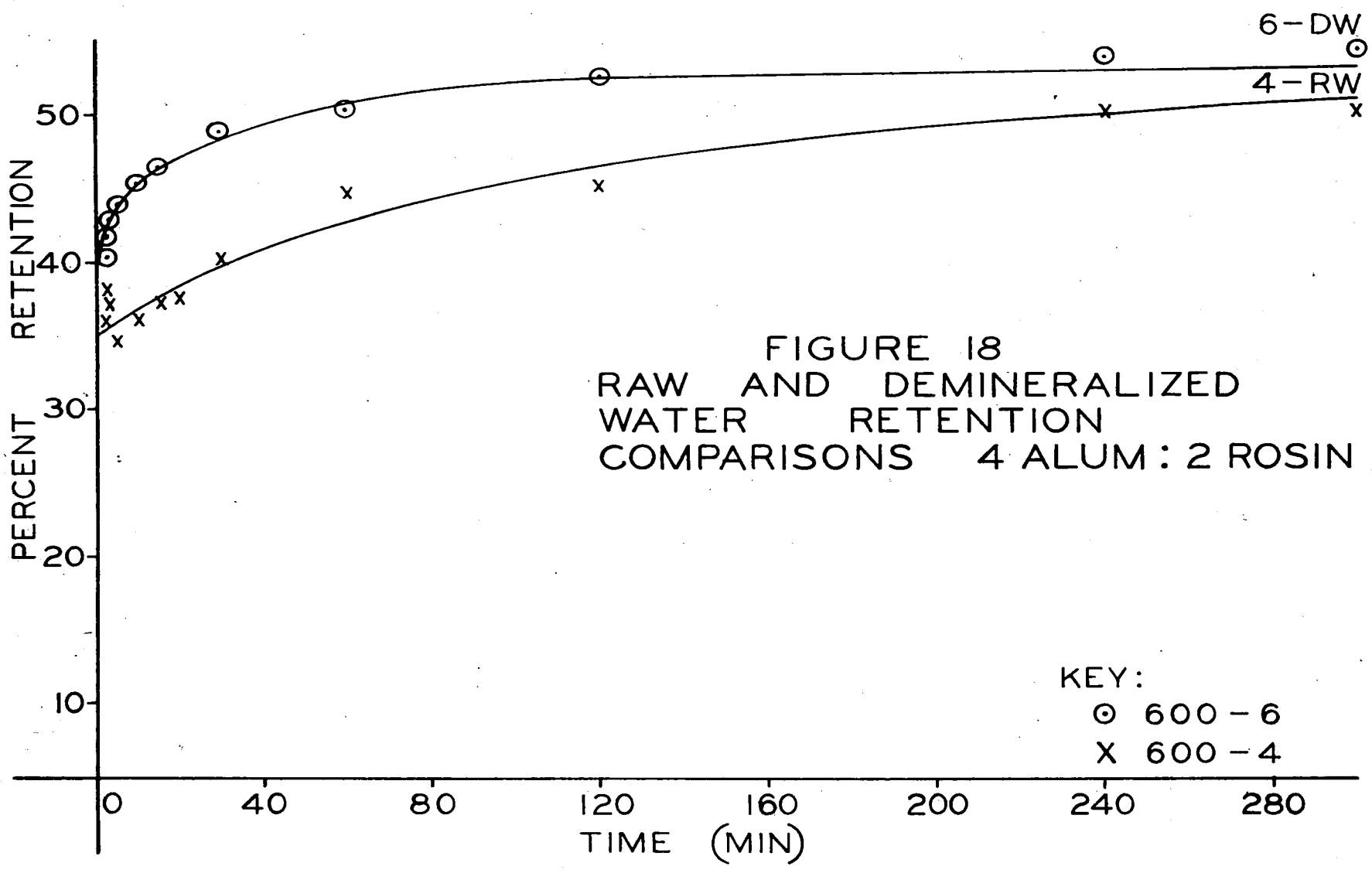


FIGURE 18
RAW AND DEMINERALIZED
WATER RETENTION
COMPARISONS 4 ALUM : 2 ROSIN

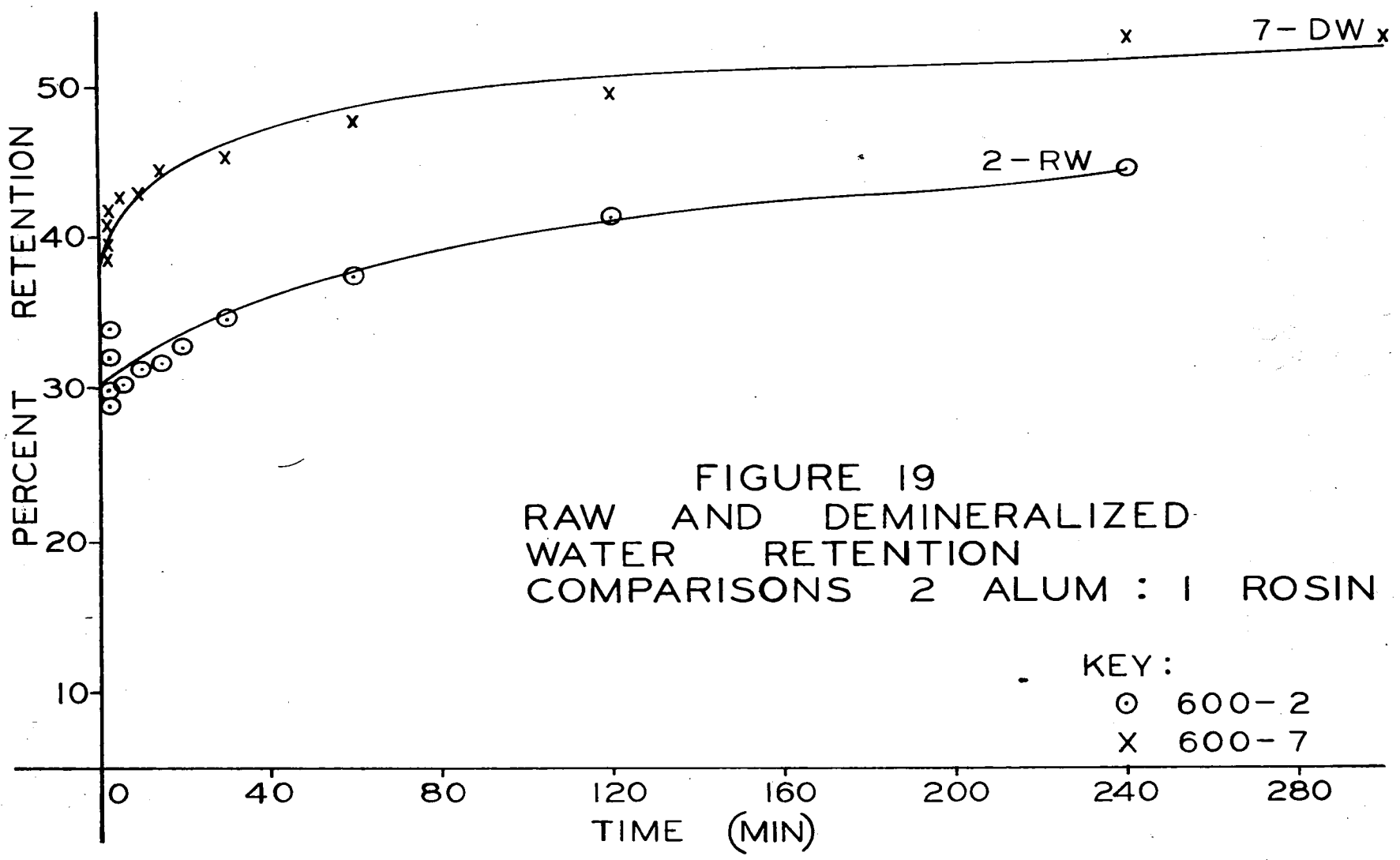


FIGURE 19
RAW AND DEMINERALIZED
WATER RETENTION
COMPARISONS 2 ALUM : 1 ROSIN

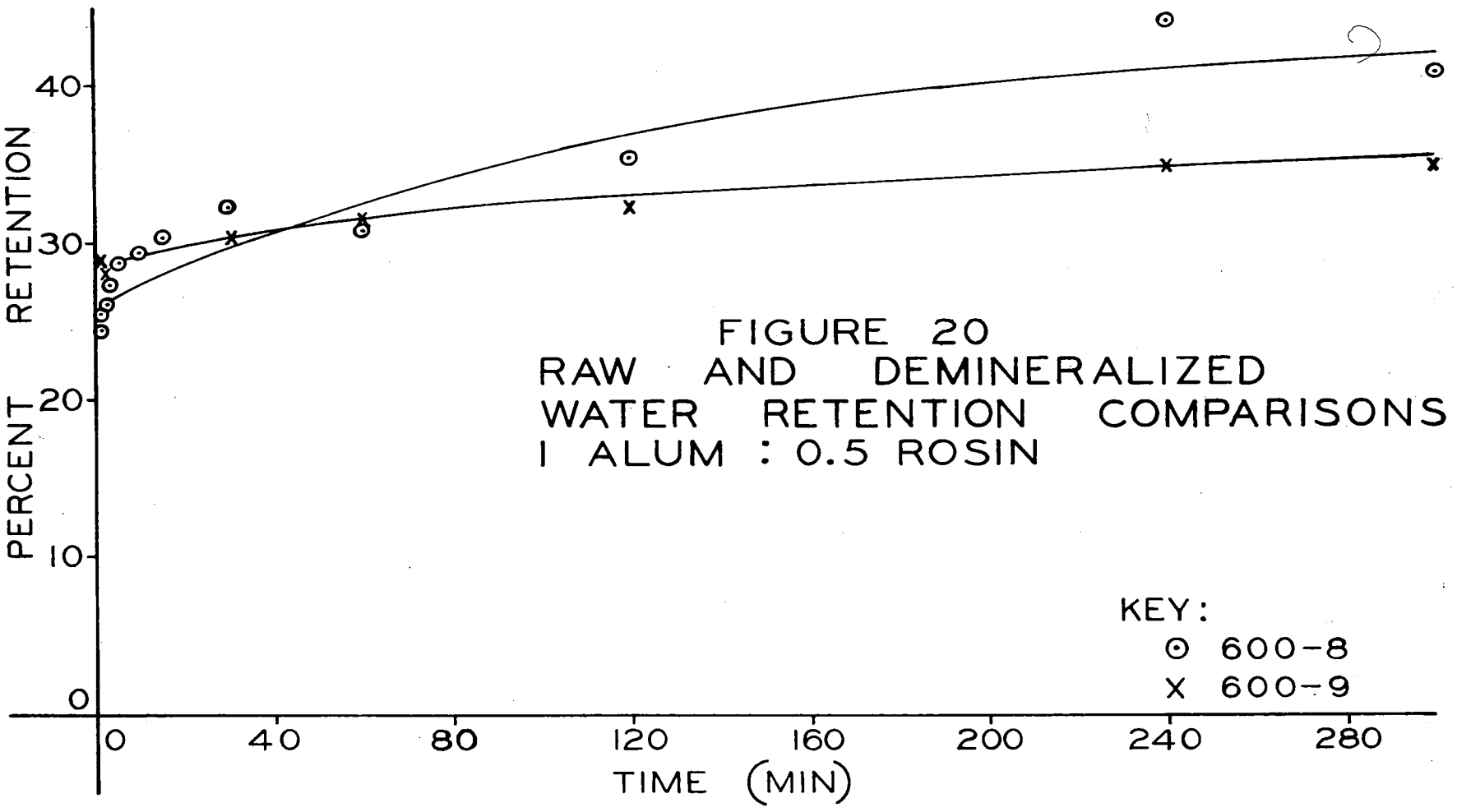


FIGURE 20
RAW AND DEMINERALIZED
WATER RETENTION COMPARISONS
1 ALUM : 0.5 ROSIN

C. Pigment to be Added to Yield Sheet with Scattering Power of 1.65 (Handsheet Test Runs)

Regression equations of pigment to be added versus time based on calculated retention and scattering coefficient results are given in Table A-XVIII. A scattering power of 1.65 was used as it was an approximate average of the experimentally obtained values.

The TiO_2 requirements to yield a sheet having a scattering power of 1.65 did not change on increasing alum concentration from 2 percent to 4 percent as illustrated in Figures 21 and 22. The requirements decreased significantly on increasing alum from 1 percent to 2 percent.

In light of the more favorable efficiency and retention found in the demineralized water systems, the pigment requirement advantage for demineralized water over raw water was expected. Table XII of Phase I shows similar results in systems with alum and rosin size.

After analyzing the individual response versus time of retention, scattering coefficient and pigment to be added, the data of PR-600-2-10 were analyzed via multiple linear regression using retention, scattering coefficient and pigment to be added as dependent variables (D_1) and the following as independent variables.

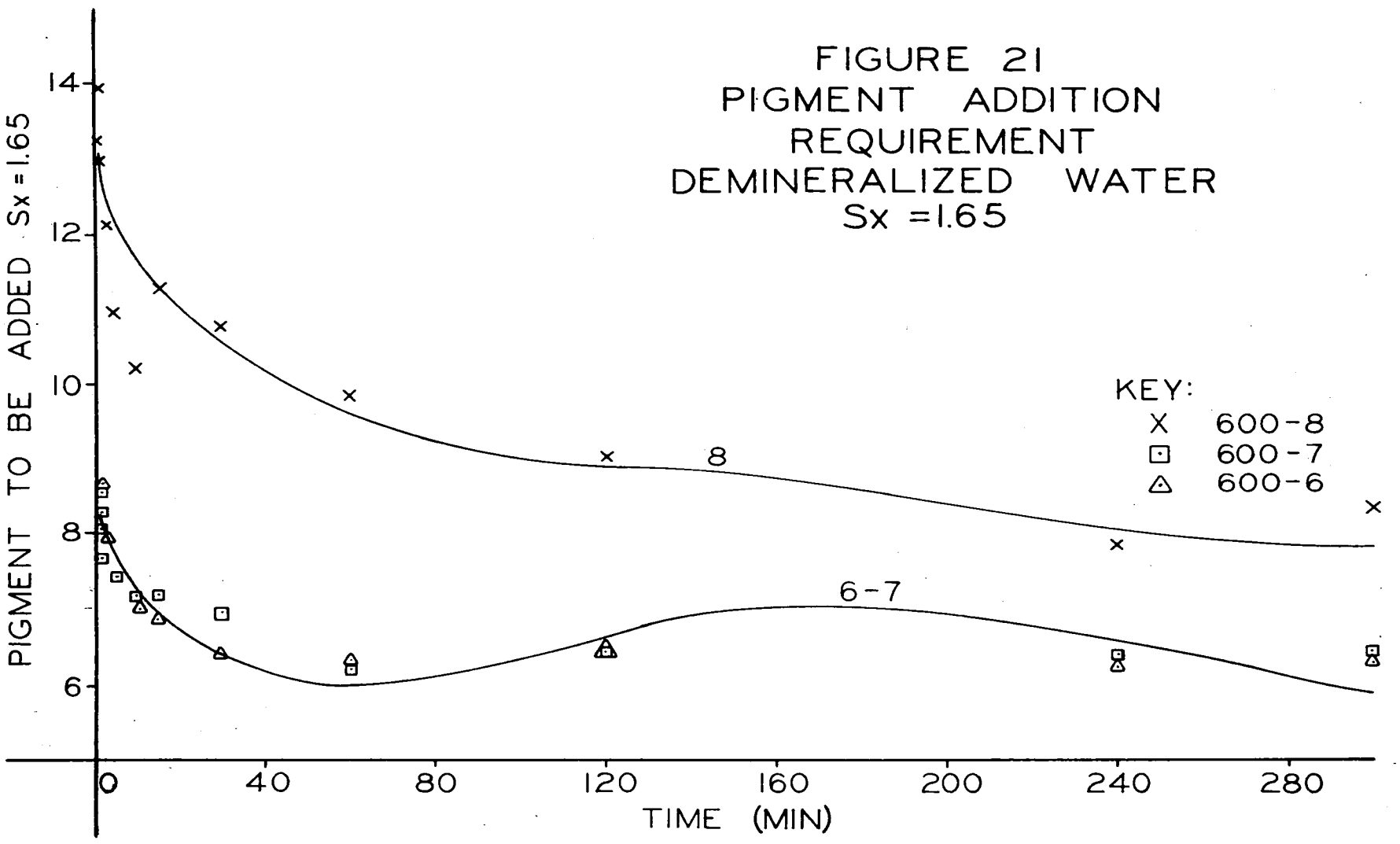


FIGURE 21
PIGMENT ADDITION
REQUIREMENT
DEMINERALIZED WATER
Sx =1.65

FIGURE 22
PIGMENT ADDITION
REQUIREMENT
RAW WATER
Sx = 1.65

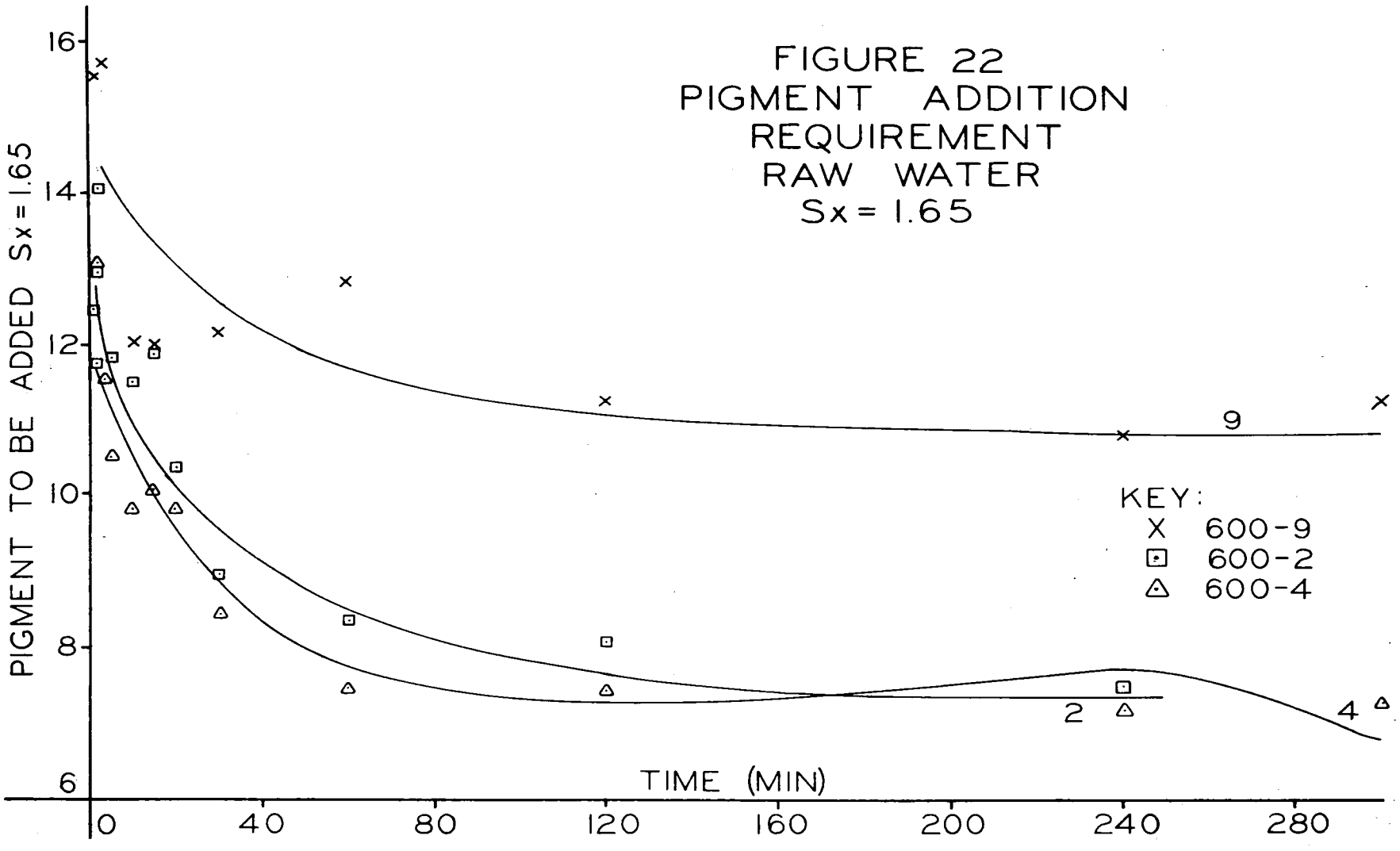


Table XIII

Variables of Multiple Linear Regression Analysis
Phase II Handsheet Test Runs

D_1 = Dependent Variable
D_2 = Time
D_3 = Alum Concentration
D_4 = Rosin Size Concentration
D_5 = Type Water
D_6 = Time x Time
D_7 = Alum x Alum
D_8 = Rosin Size x Rosin Size
D_9 = Time x Alum
D_{10} = Time x Rosin Size
D_{11} = Time x Water
D_{12} = Alum x Rosin Size
D_{13} = Alum x Water
D_{14} = Rosin x Water

Type water was denoted by +1 for raw water and -1 for demineralized water. Reaction pH was found to be insignificant in an initial analysis. After multiple runs, manipulating variables the analysis shown in:

Table A-XIX - Scattering Coefficient
Table A-XX - Retention
Table A-XXI - Pigment to be Added

gave the lowest error estimates and the following equations.

Scattering Coefficient

$$S = f(D_2, D_5, D_{11}, D_{13})$$

$$S = 0.00048t - 0.07433w + 0.0012tw + 0.0076wa + 0.734 \qquad (11)$$

Error estimate = 0.0427 (Dimensionless)

Retention

$$R = f(D_2, D_3, D_6, D_7, D_{13})$$

$$R = 0.0954t + 16.56A - 0.0016t^2 - 2.4655A^2 - 10.6553\,WA + 12.72 \qquad (12)$$

Error estimate = 2.68 percent pigment

Equations 11 and 12 will be called the composite handsheet equations (CHE) in the discussion of results.

Pigment to be Added

$$P = f(D_2, D_3, D_5, D_6, D_6, D_{11})$$

$$P = 0.0345t - 6.063A + 1.455W + 0.00007t^2 + 0.9682A^2 - 0.00249tW + 18.26 \quad (13)$$

Error estimate = 0.997 percent pigment

As shown there is marked dependency of all properties on time, type water and alum concentration. The absence of rosin size is significant in light of the earlier study which indicated marked dependency of the properties in question on its concentration.

D. Fourdrinier Program of Phase II

The data summarized in Tables A-XXII to A-XXVIII was analyzed in a similar fashion as handsheet data. Polynomial regression equations of retention and scattering coefficient versus time are given in Tables A-XXIX and A-XXX in the Appendix.

Curves (Figures 23 and 24) of these equations comparing the 4 percent alum-2 percent rosin recirculated white water run and the 2 percent alum-1 percent rosin recirculated white water run show rapidly changing end points with no indications of steady state being attained even after 4 hours. The same retention and scattering coefficient trends are shown in both systems.

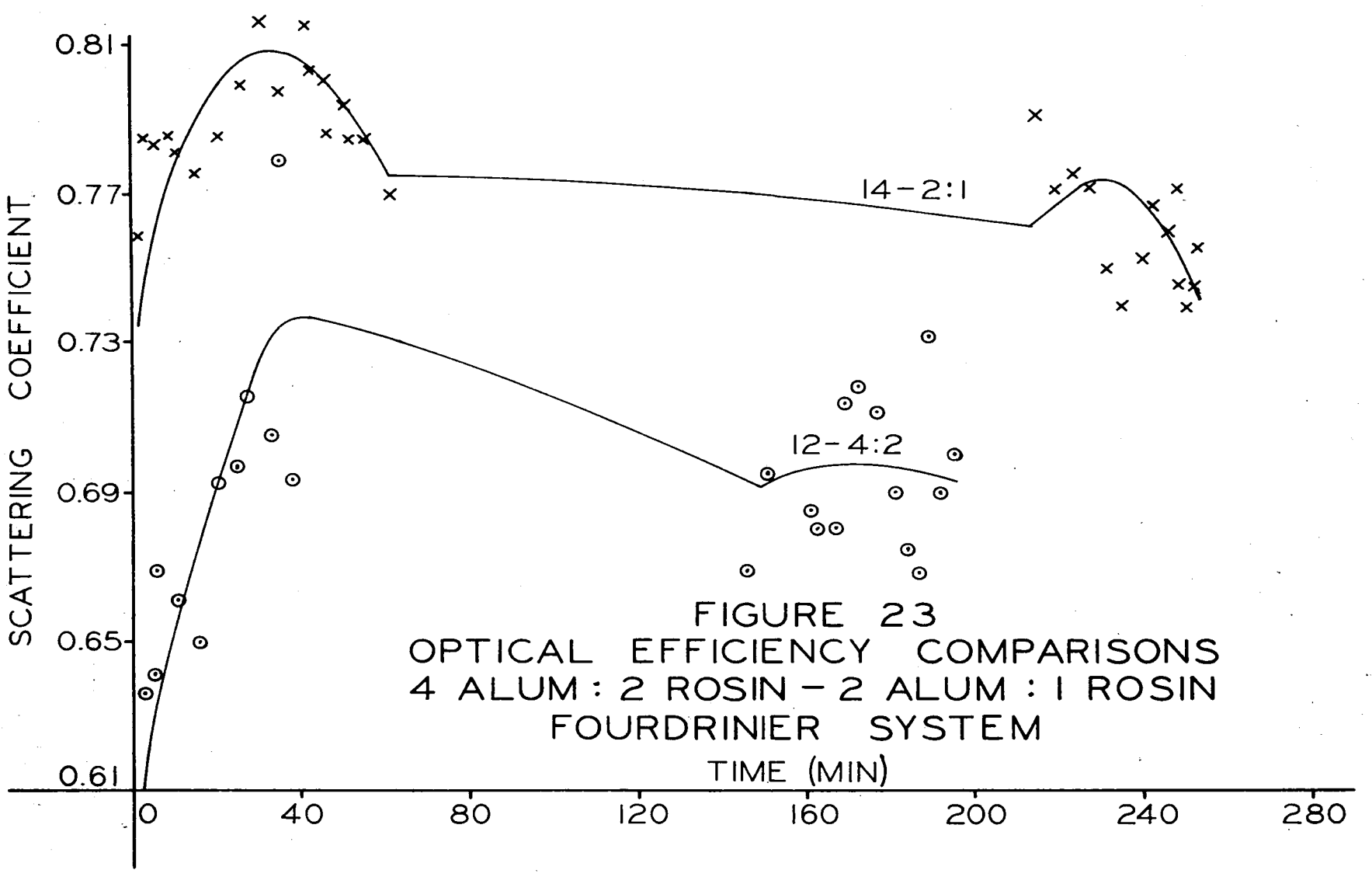
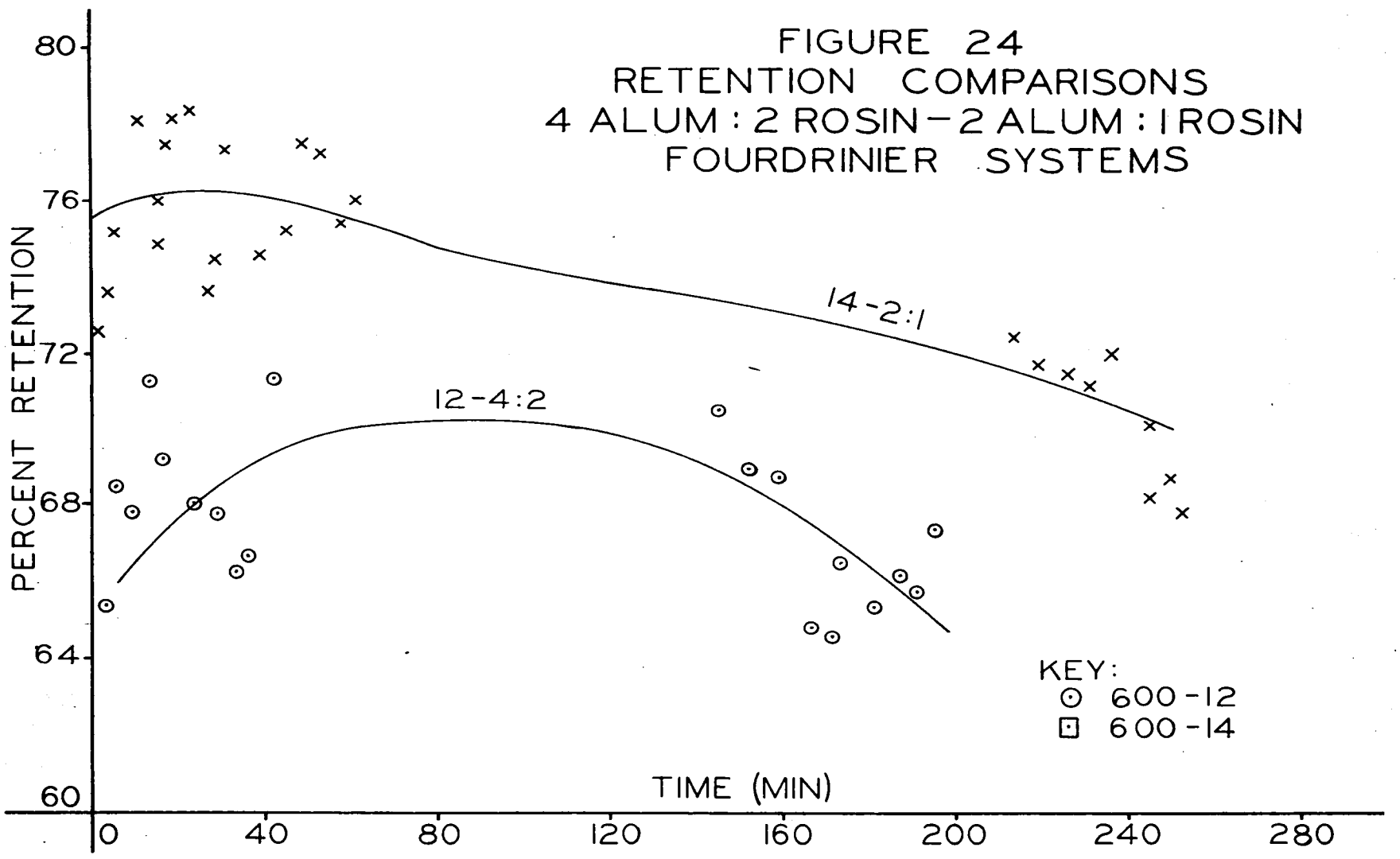


FIGURE 23
OPTICAL EFFICIENCY COMPARISONS
4 ALUM : 2 ROSIN – 2 ALUM : 1 ROSIN
FOURDRINIER SYSTEM

FIGURE 24
RETENTION COMPARISONS
4 ALUM : 2 ROSIN – 2 ALUM : 1 ROSIN
FOURDRINIER SYSTEMS



DISCUSSION OF RESULTS

I. Papermaking Variables Affecting TiO_2's Properties as a Paper Filler

One objective of this experiment was to develop a better understanding of the interactions between the common papermaking variables affecting TiO_2's optical efficiency and retention.

The variables exhibiting significant effects on TiO_2's properties in this experiment were alum concentration, type water, reaction time and rosin size concentration. Only the pH of the pulp-pigment-alum-rosin size suspension at sheet formation (Phase I) and the overall reaction pH (Handsheet Phase II) had insignificant effects.

A. Alum and Rosin Concentration

As noted earlier, there are two proposed mechanisms for the reaction between alum and rosin size. The colloidal theory states that positively charged alumina particles formed by the hydrolysis of alum attract themselves to negative pulp fibers and negative rosin particles. The ionic theory states that the alum and rosin ionize in water with the aluminum ion acting as a mutual bonding agent between the pulp and rosin precipitate. This experimental program showed that the most favorable TiO_2 retention occurred at the highest alum concentration in the handsheet phases of this program. Both the ionic theory and the colloidal theory of the alum size reaction may account for these results. As the concentration of alum is increased, the number of positively charged aluminum ions or alumina particles increase. The ions or particles

in addition to attracting themselves to the negative rosin size and pulp tend to flocculate the negatively charged TiO_2 particles. The effective particle size of TiO_2 is thus increased. Improved retention results because the larger the particle size of TiO_2 the lower the probability of it finding an opening in the fibrous mat during sheet formation, hence the filtration theory of filler retention.

Optical efficiency results showed dependency on alum concentration. Based on increased retention with increasing alum concentration, it was expected optical efficiency would decrease. A possible explanation for this effect is that the particle size distribution of TiO_2 is essentially normal. The mean size ranges from 0.25 micron to 0.30 micron, the size for optimum light scattering efficiency. If the fraction of TiO_2 particles smaller than 0.25 micron is selectively flocculated to a size of 0.25 micron to 0.30 micron by either the aluminum ion or alumina particles in the initial phases of the reaction, it would explain general retention and optical efficiency increase in this time period. Retention increase is based on filtration theory of pigment retention.

The pH behavior of the overall reaction of pulp, pigment, rosin and alum followed no consistent pattern with reference to alum and rosin. Side reactions, between rosin, alum and the other cations and anions present, were probably occurring in the raw water systems with low alum-rosin concentrations as equilibrium was not attained. At the 2 percent and 4 percent alum level, pH came to general equilibrium at 4.5 within 30 seconds. The

demineralized water runs came to equilibrium at approximately a pH of 4.0, although there was a trend toward a slight decrease with time. The reaction between alum and rosin size is given in Figure 3. The reaction shows aluminum sulfate to dissociate to aluminum ions and sulfate ions. The aluminum ions then react with water as shown below:

$$Al_2(SO_4)_3 \rightleftarrows 2Al^{+++} + 3SO_4$$

$$Al^{+++} + H_2O \rightleftarrows AlOH^{++} + H^+$$

$$AlOH^{++} + H_2O \rightleftarrows Al(OH)_2^+ + H^+$$

$$Al(OH)_2^+ + H_2O \rightleftarrows Al(OH)_3 + H^+$$

This system tends to be in equilibrium: At low hydrogen ion concentration, the formation of aluminum hydroxide is favored with a rapid drop in pH. As the pH decreases, the equilibrium shifts with an increase in the ratio of $Al^{+++}/AlOH^{++}/Al(OH)_2^+/Al(OH)_3$ until a hydrogen ion concentration is reached at which additional alum does not change pH. Thus, pH is an indirect measure of the aluminum ions and alumina particles present. Since relative equilibrium with respect to pH was attained in runs PR-600-5-8 shown in Tables A-XII to A-XV in a relatively short period of time, the aluminum ion and alumina concentration should be at equilibrium. Recalling the increasing retention results of these runs shown in Figure 16, it can be concluded that neither the concentration of aluminum ion nor alumina particles are completely responsible for the retention results.

The overall retention response in this experiment indicates that TiO_2 is probably retained according to the three

mechanisms noted earlier, as proposed by Haslam and Steele[1]. The filtration mechanism operates as there was probable flocculation of the fine particle size fraction of TiO_2 either by alumina or the aluminum ion as optical efficiency increased in initial phases of reaction. This flocculation tended to increase particle size which would aid filtration and improve retention. Mechanical attachment operates because the probability of a TiO_2 particle becoming wedged into an imperfection in a fiber surface increases with time thereby yielding higher retention. Coflocculation operates as the forces between the various components of the papermaking system interact to various degrees depending on contact time between components. As time progresses, the TiO_2 particles come in contact with all available positively charged sites on fiber resulting from reactant products of alum, rosin size and cellulose pulp.

The seven and 14 day retention and efficiency results of the Phase II Handsheet Program shown in Tables A-VIII to A-XV showed a retention increase and a marked efficiency decrease. This indicates an increase in the flocculation of TiO_2 substantiating the filtration and coflocculation mechanisms of TiO_2 retention.

B. Effect of Type Water

In this experimental program, there were retention advantages for demineralized water over raw water in all cases in which alum and rosin size were present. Without rosin and alum, the raw water system had an advantage.

An analysis of the raw water used in this investigation showed: calcium-72 ppm, magnesium-36 ppm, sodium-11 ppm,

bicarbonate-60 ppm, sulfate-53 ppm and chloride-6 ppm.

Calcium and magnesium flocculate TiO_2 and this accounts for the retention advantage for the raw water system without alum and rosin size.

In the alum and rosin systems, the anions present in the raw water deplete the residual positive charge of aluminum thereby decreasing its tendency to flocculate TiO_2. This accounts for the lower retention in raw water systems.

II. Correlation between Handsheet and Fourdrinier

The basic objective of this experimental program was to determine the degree of correlation with respect to the optical efficiency and retention properties of TiO_2 in filled paper on the two different papermaking machines. The handsheet program was conducted with both demineralized water and well water and results indicated type water to have a major effect. The Fourdrinier program was conducted using only demineralized water in order to facilitate testing. Raw water was also not used because there are inherent variations in the cation content of the well water which would affect the retention and efficiency of TiO_2 and possibly offset correlations. As noted earlier, comparisons were made at the 0, 2:1 and 4:2 alum:rosin levels with and without recirculated white water. Beater, white water lines, and machine chest addition of additives effect on TiO_2 were also compared. The Fourdrinier tests without white water recirculation were run to determine if mechanical differences between handsheet and Fourdrinier would affect properties in question. The pulp dilution procedure also differed in the handsheet and the Fourdrinier. On the handsheet, the pulp-pigment suspension was diluted both at the proportioning tank and the sheet mold with the time period between initial dilution and sheet formation approximately 1 minute. The pulp was diluted on the Fourdrinier at the headbox with sheet being formed within 10 seconds after dilution. At sheet formation, the final solids concentration in both cases was 0.2 percent solids. The initial concentration during beating was 18 percent solids so that from beating

to sheet preparation the solids were diluted to 1/90 of their original concentration. This dilution effect significantly influences the aluminum ion hydrolysis reaction (Figure 3).

A. The 4 Percent-2 Percent Rosin Size System

1. Retention - To determine the extent of differences between the handsheet and Fourdrinier systems, the regression equations given in Table A-XVII and A-XXX and Equation 12 were used to calculate retention values at various time intervals. These values are tabulated below:

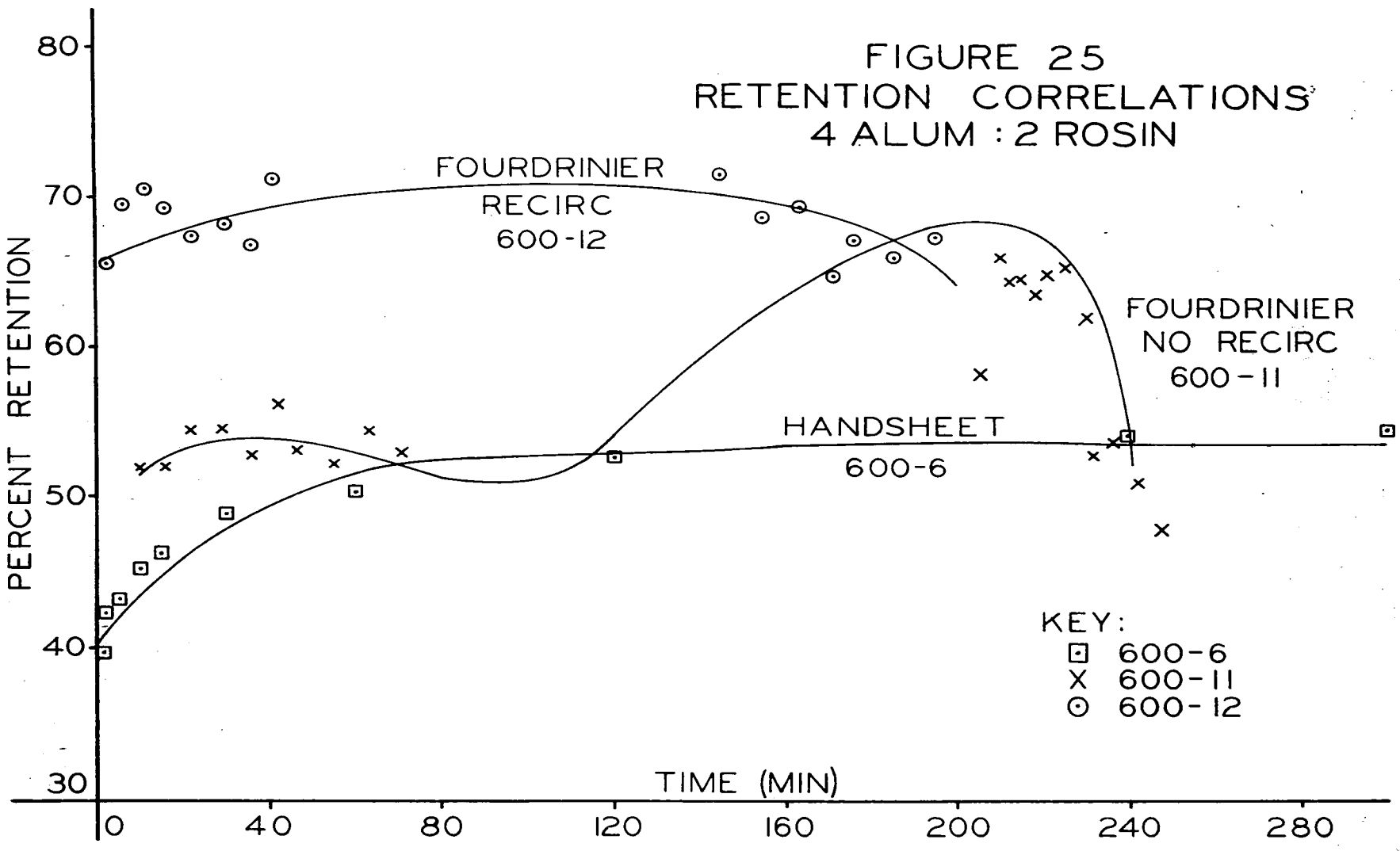
Table XIV

Retention Comparisons
Handsheet Vs. Fourdrinier

Run No.	Sheetmaking Process	Error Estimate	Percent Retention 1 Min.	10 Min.	100 Min.
600-6	Handsheet	1.06	41.6	44.1	53.2
600-11	Fourdrinier No Recirculation	2.54	49.3	51.9	50.7
600-12	Fourdrinier Recirculation	2.94	65.5	66.7	70.8
Composite Handsheet Equation (CHE) (Equation 12)		2.68	81.2	80.90	73.7

When consideration is given to the 95 percent confidence level of each of the above determinations: 600-6, ±2.28; 600-11, ±4.97; 600-12, ±5.77; and CHE, ±5.25; it is seen that the Fourdrinier results without recirculation are equal to the handsheet results at 100 minutes but are statistically marginally different at 1 minute and 10 minutes. However, from the curve (Figure 25) it is seen that there are significant differences at 150 to 230 minutes. With recirculation there is improved retention up to 140 minutes. The CHE predicts retention in a recirculated Fourdrinier run satisfactorily from 50 minutes to 150 minutes when errors are taken into consideration.

FIGURE 25
RETENTION CORRELATIONS
4 ALUM : 2 ROSIN



The process of recirculation can be thought of as a multiple pass filtration process where the coarse fraction of a suspension is selectively removed with each pass. In an attempt to determine the time interval for removal of various fraction of fines, Coulter Counter determinations were made on samples of white water taken at time intervals of 1 minute, 30 minutes and 60 minutes during the course of a Fourdrinier run. Before determinations were made, it was necessary to pass the samples through a 325 mesh screen. Results are shown below:

Table XV

Coulter Counter Determinations of White Water Fines

Time	Size Interval	Percent	Average Sizes
1 Minute	0 to 5 Microns	17	10.0 Microns
	5 to 10 "	33	
	10 to 15 "	32	
	15 "	18	
30 Minutes	0 to 5 Microns	20	9.3 Microns
	5 to 10 "	38	
	10 to 15 "	23	
	15 "	19	
60 Minutes	0 to 5 Microns	27	7.8 Microns
	5 to 10 "	37	
	10 to 15 "	26	
	15 "	10	

These results show coarse fraction to decrease with time.

Figure 22 shows a definite decrease in retention with time for both Fourdrinier runs with white water recirculation. A possible explanation of this decrease after an initial increase is that the reaction product of alum, rosin, and sulfite pulp forms a cationic product. This is indicated by zeta potential determinations showing it to have a potential of +10.6 mv. at pH of 4.4. Alum and rosin alone have a zeta potential of +16.5 at a pH of 4.3 while TiO_2 has a -5.0 potential at a pH of 4.4. Therefore, initially the negative TiO_2 is

attracted to the positively charged sites of the pulp alum-rosin mixture. As time progresses, these sites are filled with TiO_2 which has a much higher surface area than pulp.

The Coulter Counter results show a buildup of fines with time. These fines had a zeta potential of +16.2. This charge on the fines coupled with Van der Waals forces which increase as particle size decreases tended to prevent deposition of the negative TiO_2 on sites where it had been previously absorbed. The forces exerted by the fines pull the TiO_2 from the fibers and caused a decrease in retention.

The colloidal theory of rosin sizing seems to be supported by the above observations as ash analysis of the fines generally shows a majority of inorganic material. One explanation for the +16.2 mv. charge of the fines in comparison to -5.0 for TiO_2 is that positively charged alumina is precipitated on the TiO_2.

Another possible reason for the retention decrease is that as time progresses there is a buildup of sulfate ions in the white water from the alum as the sulfate ion is not a part of the size precipitate. The sulfate ion being a strong electrolyte tends to collapse all charges toward the establishment of an isoelectric condition.[15] Therefore, the highly positive alumina and aluminum ions become less positive and the negative TiO_2 becomes less negative. Electrokinetic forces attracting these materials thus decrease resulting in retention losses.

The buildup of sulfate ions with time may account for the retention differences between handsheet and Fourdrinier run without recirculation. More complete hydrolysis of the aluminum ion (Figure 3) occurs in the handsheet run than in the Fourdrinier run because of the time differences in the dilution procedure. The resulting higher sulfate ion concentration in the handsheet run tends to lower TiO_2 retention as previously described.

For the Fourdrinier run without recirculation, the decrease in retention after an initial increase cannot be explained from available information.

2. Scattering Coefficient - Comparisons of scattering coefficients are shown in Figure 26 and in Table XVI below:

Table XVI

Scattering Coefficient Comparisons
4 Alum:2 Rosin Size System of Phase II

Run No.	Sheetmaking Process	Error Estimate	Scattering Coefficient 1 Min.	10 Min.	100 Min.
600-6	Handsheet	0.022	0.780	0.802	0.816
600-11	Fourdrinier No Recirculation	0.053	0.686	0.688	0.691
600-12	Fourdrinier Recirculation	0.043	0.589	0.648	0.734
CHE (Equation 11)		0.043	0.777	0.770	0.706

Confidence limits (95 percent) of each determination are 600-6, ±0.047; 600-11, ±0.104; 600-12, ±0.085 and CHE, 0.084. Mechanical differences between handsheet and Fourdrinier had no effect on optical efficiency based on handsheet and non-recirculated Fourdrinier results. The differences between the Fourdrinier systems were also insignificant.

A potential pitfall in handsheet testing occurs when comparing the coefficients in handsheet to recirculated Fourdrinier calculated in the first 20 minutes. This shows a higher scattering coefficient of TiO_2 in the one-pass handsheet system. If a mill is using a handsheet test to determine possible TiO_2 addition level changes in their formulations for given optical properties, low estimates of TiO_2 needed will result if the reaction of pigment, alum, rosin and pulp is not conducted for at least 20 minutes. The CHE recirculation Fourdrinier comparisons illustrate this effect. Paper which does not meet optical specifications may be produced on the

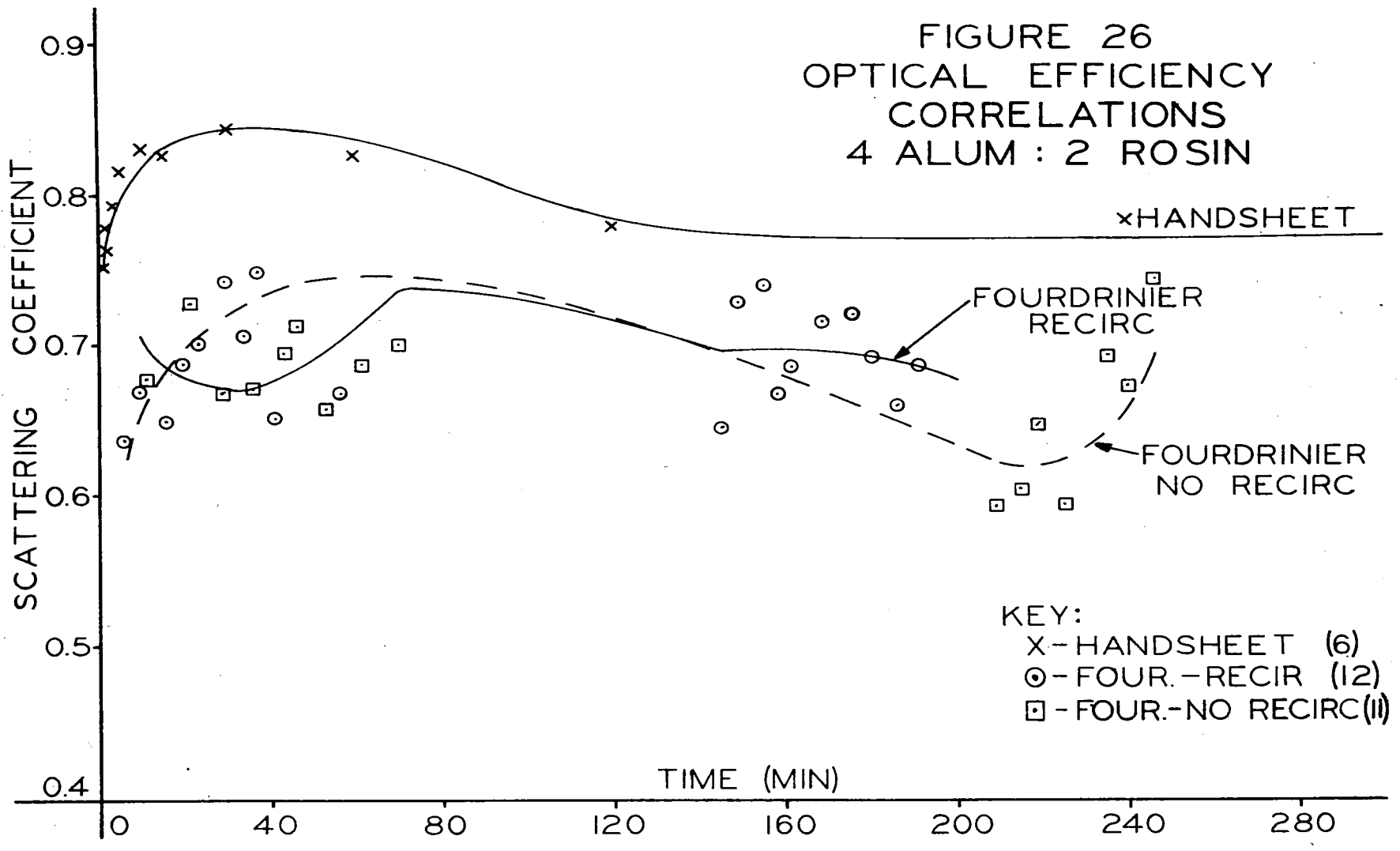


FIGURE 26
OPTICAL EFFICIENCY
CORRELATIONS
4 ALUM : 2 ROSIN

Fourdrinier if handsheet information is used in formulation changes.

B. The 2 Percent Alum-1 Percent Rosin Size System

1. Retention - Retention results for the three test runs at selected time intervals are tabled below:

Table XVII

Retention Comparisons
2 Alum:1 Rosin Size System of Phase II

Run No.	Sheetmaking Process	Error Estimate	Percent Retention 1 Min.	10 Min.	100 Min.
600-7	Handsheet	1.14	40.4	42.6	50.8
600-13	Fourdrinier No Recirculation	4.63	44.1	51.6	49.8
600-14	Fourdrinier Recirculation	1.86	75.9	76.0	75.5
CHE (Equation 12)		2.68	58.2	58.1	41.2

Curves of the above test runs are given in Figure 27. Confidence limits: 600-7, ±2.65; 600-13, ±9.1; 600-14, ±3.64 and CHE, ±5.25.

There are no differences between the handsheet and Fourdrinier run with no recirculation, with both systems showing significantly lower retention than the other Fourdrinier runs. The CHE is unsatisfactory for predicting retention values in this alum, rosin system. The relative retention response of all tests at this alum and rosin size concentration followed the same trend as the 4 alum:2 rosin system as shown in Figure 24. Both systems showed an initial retention increase followed by a decrease.

2. Scattering Coefficient - Scattering coefficients comparisons for the 2 alum:1 rosin system are tabled below:

Table XVIII

Scattering Coefficient Comparisons
2 Alum:1 Rosin System of Phase II

Run No.	Sheetmaking Process	Error Estimate	Scattering Coefficient 1 Min.	10 Min.	100 Min.
600-7	Handsheet	0.024	0.772	0.781	0.791
600-13	Fourdrinier No Recirculation	0.044	0.795	0.776	0.775
600-14	Fourdrinier Recirculation	0.038	0.750	0.760	0.819
CHE		0.043	0.792	0.786	0.706

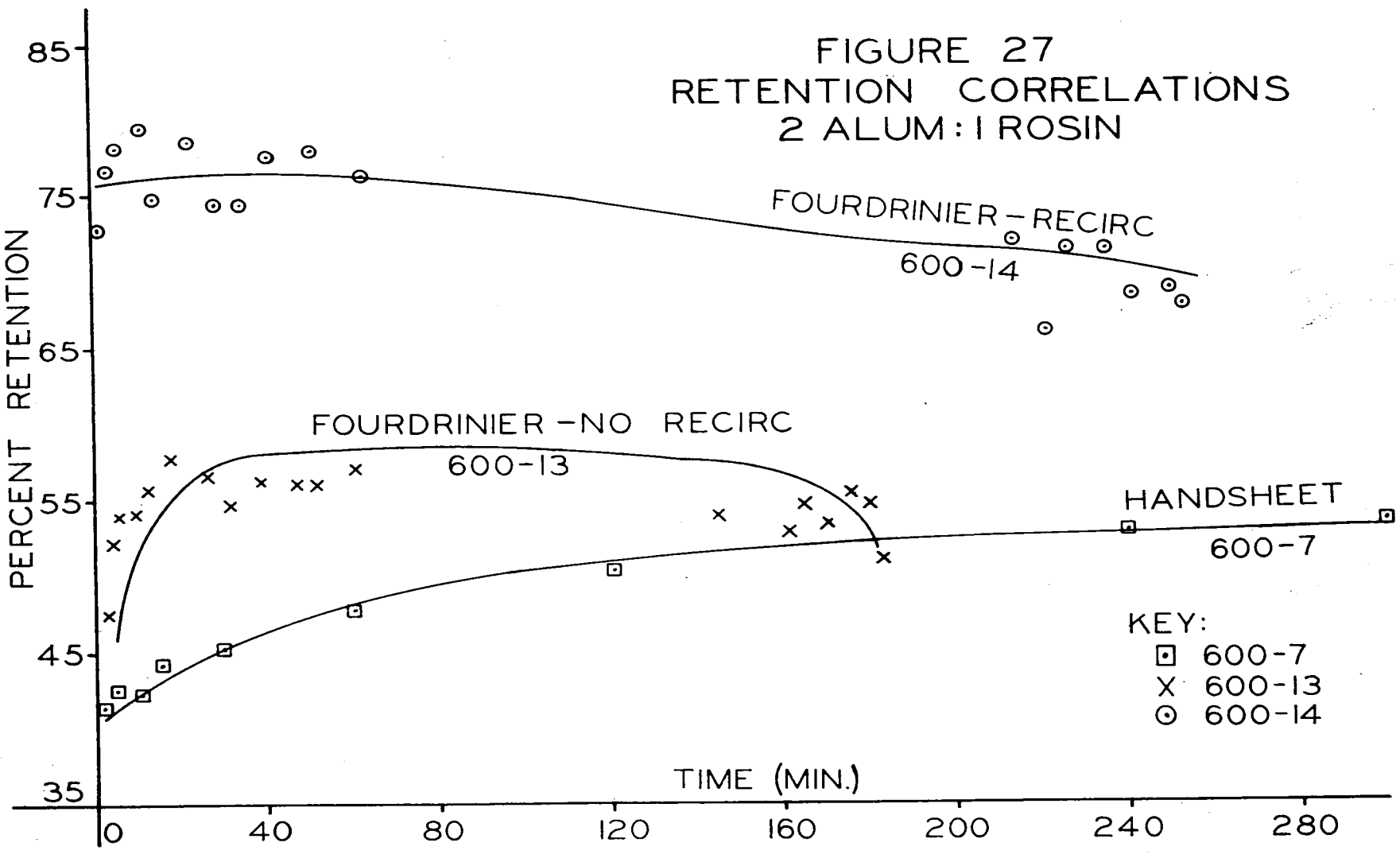
Confidence limits: 600-7, $\pm$0.052; 600-13, $\pm$0.086; 600-14, $\pm$0.075 and CHE, $\pm$0.084.

Based on these results, there are no significant differences in the values shown for the different processes. This is in direct contrast to the 4 alum:2 rosin system. These differences in the degree of correlation further substantiate the original handsheet test results which showed the dependency of the scattering coefficient and retention on alum and rosin size concentration.

The lower retention of the 4 alum:2 rosin system in comparison to the 2 alum:1 rosin system in the recirculated Fourdrinier is different from the retention response in the handsheet program which showed increased retention with increasing alum concentration. This difference is probably explained by the sulfate ion concentration differences in the white water at the two alum concentrations. At 2 percent alum, the concentration of the sulfate ion in the white water is probably not sufficient to collapse the positive charge of the alumina particles and the aluminum ion, which are responsible for flocculating TiO_2, hence higher TiO_2 retention is shown at the 2 percent alum level.

A possible explanation for the higher scattering coefficients in the 2 alum:1 rosin system than in the 4 alum:2 rosin system is

FIGURE 27
RETENTION CORRELATIONS
2 ALUM : 1 ROSIN



that different pigment floc sizes are formed at the two alum concentrations. The floc size range in the 2 alum:1 rosin system may be more efficient for light scattering.

III. Effect of Variations in Location of Alum Addition System - 2 Alum:1 Rosin

Presently in commercial practice, there are a number of locations in a papermaking system in which alum is added:

1. Beater
2. Machine Chest of Fourdrinier
3. White Water Recirculating Line of Fourdrinier

In this experiment the effect of these differences on the retention and optical properties of TiO_2 was evaluated. Alum was added in the recirculating ling in PR-600-16 and all additives were added at the beater in PR-600-17. Order of addition of additives in 600-17 was similar to previous runs, i.e., pulp, pigment, rosin and alum. Comparison of results are given in Tables XIX and XX.

Table XIX

Scattering Coefficient Comparisons - Variations in Location of Additive Addition - 2 Alum:1 Rosin System

Run No.	Location	Error Estimate	Scattering Coefficient 1 Min.	10 Min.	100 Min.
600-14	Machine Chest	0.043	0.750	0.760	0.819
600-16	Recirculating Line	0.035	0.720	0.761	0.68
600-17	Beater	No Correlation			

From the above scattering coefficient is independent of location of alum addition. One should remember that only one order of addition was tested and in the earlier run, there was a dependency of optical efficiency on order of addition of additives.

The scattering coefficient in PR-600-16, illustrated in

Figure 28, shows an initial increase then a sharp decrease. This can be explained by the flocculating effect of alum. As the alum concentration in the white water system increases, it tends to increase effective size of TiO_2 from below optimum for maximum optical efficiency to above optimum size. Optimum efficiency was shown at 20-30 minutes in this experiment.

Table XX

Retention Comparisons - Variations in Location of Additive Addition - 2 Alum:1 Rosin System

Run No.	Location	Error Estimate	Retention 1 Min.	10 Min.	100 Min.
600-14	Machine Chest	1.86	75.9	76.0	75.5
600-16	Recirculating Line	No Correlation			
600-17	Beater (1)	3.51	70.5	65.6	66.4
	(2)	3.51	-	-	62.3

Two values are reported for 600-17: (1) Based on actual Fourdrinier running time and (2) based on beating time (76 minutes) and Fourdrinier running time. The 95 percent confidence limits are 600-14, $\pm$3.64 and 600-17, $\pm$7.16. Retention response is thus the same in the two systems. While unsatisfactory correlation was found in 600-16, it should be noted that experimental values generally were within confidence limits of the other two runs.

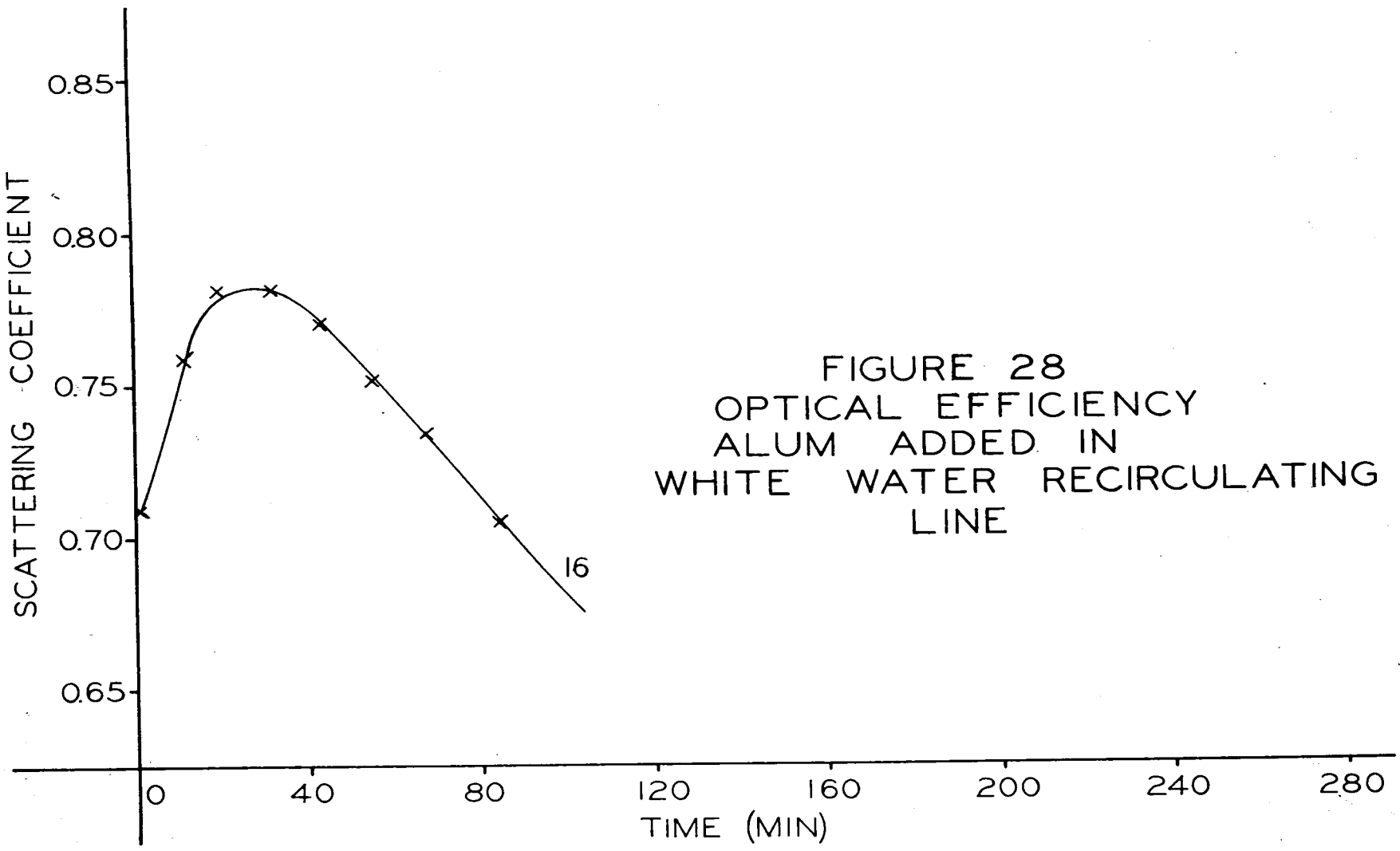


FIGURE 28
OPTICAL EFFICIENCY
ALUM ADDED IN
WHITE WATER RECIRCULATING
LINE

SUMMARY AND CONCLUSIONS

This program was conducted to study the effect of alum concentration, rosin size concentration, type water, pH of papermaking system, pH of reaction, and order of additive addition on the optical efficiency and retention properties of TiO_2 on a laboratory Fourdrinier and on a handsheet machine and to show correlations between these two papermaking systems. By studying these variables, it was hoped that a better understanding would result of the mechanism of TiO_2 retention and optical efficiency in filled paper.

The following are most significant results:

1. The variables exhibiting significant effects on TiO_2's properties in this program were alum concentration, type water, reaction time, and rosin size concentration. A number of interactions between these variables namely: water-alum, water-alum-rosin, and time-alum also had significant effects.

2. No firm conclusions on the mechanism of TiO_2 retention could be made based on this experiment, but results indicate it probably is a combination of filtration, mechanical attachment and co-flocculation.

3. Optical efficiency comparisons in the various phases of this program were not consistent with the variables studied. In the handsheet program, highest efficiency was shown in the 1 alum:0.5 rosin and 4 alum:2 rosin systems while the Fourdrinier phase TiO_2 exhibited highest efficiency in the 2 alum:1 rosin system.

4. The degree of correlation in retention and optical efficiency between the handsheet and Fourdrinier was dependent on reaction time and alum and rosin size concentration.

5. Variation in the location of alum addition in the Fourdrinier papermaking system has no significant effect on the retention and scattering coefficient of TiO_2.

6. Mechanical and pulp dilution differences, neglecting white water recirculation, between the handsheet and the Fourdrinier had only minor effects on the properties studied.

7. The experimental work in this program suggests that the Coulter Counter and the Zeta Meter may be useful tools in understanding the mechanism of pigment retention and optical efficiency.

Overall the complicated interactions detected between the papermaking systems indicate that further work is needed in the development of a meaningful laboratory paper filler test method.

RECOMMENDATIONS FOR FUTURE WORK

A number of areas for future study were suggested by this program.

1. The use of the Coulter Counter and the Zeta Meter, studying the change in the size and charge with time under different papermaking conditions of the fines in the white water may give a better understanding of the mechanism of pigment retention and efficiency.

2. Chemical analysis of the white water determining the concentration of aluminum resinate, alumina, TiO_2 and $SO_4^=$ at various time periods will possibly explain retention and scattering coefficient differences at the different alum and rosin size concentrations.

3. The extent of selective flocculation proposed as one of the mechanisms for the optical efficiency response in various phases of this program, can be studied by particle size distribution determinations of TiO_2 flocculated with different concentrations of alum.

4. Surface replicas of TiO_2 filled sheets prepared under different conditions while tedious and expensive will show distribution of TiO_2 in the sheet and possibly help explain relative retention and scattering coefficient results of this program.

APPENDIX

Tables A-I to A-XXX

TABLE A-I

Phase I

Block Diagram of Experiment

pH 4.5		pH 5.5		pH 6.5				
1% Alum	2% Alum	1% Alum	2% Alum	1% Alum	2% Alum			
3-1	1-1	3-2	1-2	3-3	1-3	0 Size	Raw H_2O	Order A
4-1	2-1	4-2	2-2	4-3	2-3	1% Size		
1-4	3-4	1-5	3-5	1-6	3-6	0 Size	Dim H_2O	
2-4	4-4	2-5	4-5	2-6	4-6	1% Size		
3-7	1-7	3-8	1-8	3-9	1-9	0 Size	Raw H_2O	Order B
4-7	2-7	4-8	2-8	4-9	2-9	1% Size		
1-10	3-10	1-11	3-11	1-12	3-12	0 Size	Dim H_2O	
2-10	4-10	2-11	4-11	2-12	4-12	1% Size		
3-13	1-13	3-14	1-14	3-15	1-15	0 Size	Raw H_2O	Order C
4-13	2-13	4-14	2-14	4-15	2-15	1% Size		
1-16	3-16	1-17	3-17	1-18	3-18	0 Size	Dim H_2O	
2-16	4-16	2-17	4-17	2-18	4-18	1% Size		

TABLE A-II

Phase I

Summary of Calculated Results

Sample Code	Scattering Coefficient	% TiO_2 Retention
*1- 1	0.818	29.44
1- 2	0.776	32.15
1- 3	0.788	32.41
1- 4	0.652	39.89
1- 5	0.664	38.72
1- 6	0.679	35.83
1- 7	0.664	23.30
1- 8	0.605	27.95
1- 9	0.650	25.60
1-10	0.535	32.16
1-11	0.559	27.54
1-12	0.556	26.40
1-13	0.697	31.82
1-14	0.620	24.70
1-15	0.719	35.88
1-16	0.643	47.62
1-17	0.732	39.45
1-18	0.673	42.27

Notes: *Denotes experiment number given in Table A-I.

TABLE A-III

Phase I

Summary of Calculated Results

Sample Code	Scattering Coefficient	% TiO_2 Retention
*2- 1	0.823	28.50
2- 2	0.879	31.84
2- 3	0.807	32.33
2- 4	0.812	38.84
2- 5	0.830	37.58
2- 6	0.807	38.69
2- 7	0.769	28.09
2- 8	0.770	26.57
2- 9	0.788	27.00
2-10	0.796	36.35
2-11	0.813	35.37
2-12	0.849	31.37
2-13	0.794	32.73
2-14	0.810	33.17
2-15	0.817	33.43
2-16	0.786	42.42
2-17	0.781	41.46
2-18	0.792	39.34

Notes: *Denotes experiment number given in Table A-I.

TABLE A-IV

Phase I

Summary of Calculated Results

Sample Code	Scattering Coefficient	% TiO_2 Retention
*3- 1	0.942	27.07
3- 2	0.926	27.12
3- 3	0.971	25.65
3- 4	0.751	38.40
3- 5	0.789	37.47
3- 6	0.718	43.26
3- 7	0.916	23.36
3- 8	0.950	22.55
3- 9	0.918	20.47
3-10	0.671	33.41
3-11	0.653	35.71
3-12	0.665	37.29
3-13	0.974	27.21
3-14	0.977	26.57
3-15	0.974	24.56
3-16	0.754	37.91
3-17	0.660	42.41
3-18	0.692	44.74

Notes: *Denotes experiment number given in Table A-I.

TABLE A-V

Phase I

Summary of Calculated Results

Sample Code	Scattering Coefficient	% TiO_2 Retention
*4- 1	0.901	30.28
4- 2	0.922	31.29
4- 3	0.924	29.81
4- 4	0.833	40.92
4- 5	0.814	44.64
4- 6	0.828	45.36
4- 7	0.922	23.15
4- 8	0.867	24.54
4- 9	0.883	24.78
4-10	0.818	38.54
4-11	0.833	41.34
4-12	0.817	41.96
4-13	0.813	31.14
4-14	0.832	32.26
4-15	0.831	32.21
4-16	0.776	39.31
4-17	0.763	43.49
4-18	0.739	46.40

Notes: *Denotes experiment number given in Table A-I.

TABLE A-VI

Phase I

Analysis of Variance
Scattering Coefficient

Source of Variation	Sums of Squares	Degrees of Freedom	Variance
A	693.160	1	693.160
H	0.756	2	0.378
AH	30.997	2	15.498
S	1018.508	1	1018.508
AS	104.642	1	104.642
HS	6.876	2	3.438
AHS	41.166	2	20.583
W	1705.279	1	1705.279
AW	1666.568	1	1666.568
HW	10.265	2	5.132
AHW	12.746	2	6.373
SW	656.426	1	656.426
ASW	720.733	1	720.733
HSW	18.896	2	9.448
AHSW	5.256	2	2.628
O	427.738	2	213.869
AO	74.025	2	37.012
HO	10.567	4	2.641
AHO	41.272	4	10.318
SO	306.444	2	153.222
ASO	111.953	2	55.976
HSO	5.930	4	1.482
AHSO	35.562	4	8.890
WO	11.910	2	5.955
AWO	103.005	2	51.502
HWO	16.483	4	4.120
AHWO	18.363	4	4.590
SWO	45.983	2	22.991
ASWO	60.709	2	30.354
HSWO	21.182	4	5.295
AHSWO Residual	28.493	4	7.123
Total	8011.899	71	

TABLE A-VII

Phase I

Analysis of Variance
TiO_2 Retention

Source of Variation	Sums of Squares	Degrees of Freedom	Variance
A	180.975	1	180.975
H	5.152	2	2.576
AH	106.277	2	53.138
S	108.069	1	108.069
AS	0.302	1	0.302
HS	10.648	2	5.324
AHS	10.871	2	5.435
W	2036.601	1	2036.601
AW	0.973	1	0.973
HW	0.646	2	0.323
AHW	33.978	2	16.989
SW	0.080	1	0.080
ASW	27.269	1	27.269
HSW	1.604	2	0.802
AHSW	2.448	2	1.224
O	571.497	2	285.748
AO	32.354	2	16.177
HO	19.166	4	4.791
AHO	4.212	4	1.053
SO	12.108	2	6.054
ASO	0.161	2	0.080
HSO	10.974	4	2.743
AHSO	9.067	4	2.266
WO	11.440	2	5.720
AWO	26.544	2	13.272
HWO	6.592	4	1.648
AHWO	23.035	4	5.758
SWO	47.984	2	23.992
ASWO	14.395	2	7.197
HSWO	6.356	4	1.589
AHSWO Residual	28.644	4	7.161
Total	3350.431	71	

TABLE A-VIII

Summary of PR-600-10 Calculated Results and Reaction pH Values

Time (Min.)	Scattering Coefficient	% TiO_2 Retention	% Pigment Required in Sheet for Sx=1.65	% Pigment to be Added Sx=1.65	pH of Reaction
15 Sec.	0.678	26.2	3.94	15.05	8.0
30	0.672	26.1	3.98	15.25	8.0
1 Min.	0.674	26.4	3.97	15.02	7.5
2	0.677	26.3	3.95	15.01	7.6
3	0.674	26.3	3.97	15.10	7.6
5	0.679	26.0	3.94	15.14	7.7
10	0.704	25.7	3.79	14.75	7.7
15	0.685	25.5	3.90	15.29	7.8
30	0.684	25.8	3.91	15.14	7.8
60	0.685	25.9	3.90	15.06	8.1
120	0.706	26.1	3.78	14.48	8.3
240	0.687	26.3	3.89	14.78	8.3
300	0.653	24.8	4.10	16.53	8.2
360	0.650	25.1	4.12	16.41	8.3
7 Days	0.438	75.2	6.25	8.32	6.1
14	0.440	66.3	6.23	9.39	6.7

Conditions: No Alum
No Rosin Size
Raw Water

TABLE A-IX

Summary of PR-600-9 Calculated Results and Reaction pH Values

Time (Min.)	Scattering Coefficient	% TiO_2 Retention	% Pigment Required in Sheet for Sx=1.65	% Pigment to be Added Sx=1.65	pH of Reaction
15 Sec.	0.594	29.0	4.50	15.52	5.8
30	0.663	28.6	4.01	14.02	5.9
1 Min.	0.674	28.1	3.94	14.02	5.9
2	0.656	28.5	4.05	14.21	6.0
3	0.611	27.8	4.37	15.71	6.1
5	0.640	28.7	4.16	14.55	6.4
10	0.745	29.5	3.55	12.03	6.8
15	0.735	30.0	3.60	12.00	7.0
30	0.717	30.3	3.70	12.19	7.2
60	0.664	31.2	4.00	12.83	7.3
120	0.729	32.3	3.63	11.24	7.3
240	0.710	34.6	3.73	10.79	7.3
300	0.674	34.9	3.94	11.29	7.3
360	0.691	35.8	3.84	10.73	7.3
7 Days	0.493	77.6	5.48	7.06	5.6
14	0.468	66.9	5.79	12.38	6.2

Conditions: 1% Alum
1/2% Rosin Size
Raw Water

TABLE A-X

Summary of PR-600-2 Calculated Results and Reaction pH Values

Time (Min.)	Scattering Coefficient	% TiO_2 Retention	% Pigment Required in Sheet for Sx=1.65	% Pigment to be Added Sx=1.65	pH of Reaction
15 Sec.	0.588	34.2	4.26	12.45	4.7
30	0.664	32.2	3.75	11.63	4.5
1 Min.	0.637	30.2	3.91	12.95	4.5
2	0.604	29.4	4.14	14.07	4.5
3	0.678	30.3	3.66	12.09	4.5
5	0.694	30.2	3.58	11.84	4.5
7.5	0.727	31.0	3.41	10.99	4.5
10	0.694	31.1	3.58	11.50	4.5
15	0.659	31.7	3.78	11.91	4.5
20	0.728	32.8	3.40	10.37	4.5
30	0.791	34.8	3.12	8.97	4.5
60	0.792	37.5	3.12	8.31	4.5
120	0.745	41.3	3.32	8.04	4.5
240	0.746	44.3	3.32	7.49	4.5

Conditions: 2% Alum
1% Rosin Size
Raw Water

TABLE A-XI

Summary of PR-600-4 Calculated Results and Reaction pH Values

Time (Min.)	Scattering Coefficient	% TiO_2 Retention	% Pigment Required in Sheet for Sx=1.65	% Pigment to be Added Sx-1.65	pH of Reaction
15 Sec.	0.624	37.6	4.26	11.60	4.4
30	0.653	35.8	4.16	11.61	4.4
1 Min.	0.632	36.5	4.30	11.79	4.4
2	0.613	34.0	4.44	13.06	4.4
3	0.671	34.8	4.04	11.61	4.4
5	0.745	34.6	3.62	10.47	4.4
10	0.756	36.4	3.57	9.80	4.4
15	0.719	37.5	3.76	10.02	4.4
20	0.732	37.7	3.69	9.79	4.4
30	0.786	40.4	3.43	8.48	4.4
1 Hr.	0.808	44.6	3.33	7.47	4.4
2	0.767	45.4	3.51	7.72	4.4
4	0.752	50.2	3.59	7.15	4.4
5	0.744	50.1	3.63	7.24	4.4
6	0.755	51.8	3.57	6.90	4.4

Conditions: 4% Alum
2% Rosin Size
Raw Water

TABLE A-XII

Summary of PR-600-5 Calculated Results and Reaction pH Values

Time (Min.)	Scattering Coefficient	% TiO_2 Retention	% Pigment Required in Sheet for Sx=1.65	% Pigment to be Added Sx=1.65	pH of Reaction
15 Sec.	0.858	9.8	3.04	31.0	6.6
30	0.865	10.3	3.01	29.25	6.6
1 Min.	0.765	10.2	3.42	33.56	6.6
2	0.811	10.2	3.22	31.59	6.6
3	0.855	10.9	3.05	27.98	6.6
5	0.842	10.7	3.10	28.96	6.7
10	0.733	10.9	3.58	32.83	6.7
15	0.838	11.9	3.11	26.17	6.7
30	0.859	12.3	3.04	24.67	6.7
60	0.830	12.1	3.15	25.99	6.7
105	0.685	11.9	3.84	32.28	6.7
240	0.753	12.1	3.48	28.76	6.7
300	0.753	11.9	3.48	29.24	6.7
360	0.791	11.7	3.31	28.26	6.7
7 Days	0.631	15.0	4.19	27.91	5.7
14	0.508	33.8	5.26	15.57	5.7

Conditions: No Alum
No Rosin Size
Demineralized Water

TABLE A-XIII

Summary of PR-600-8 Calculated Results and Reaction pH Values

Time (Min.)	Scattering Coefficient	% TiO_2 Retention	% Pigment Required in Sheet for Sx=1.65	% Pigment to be Added Sx=1.65	pH of Reaction
15 Sec.	0.781	24.4	3.41	13.96	4.4
30	0.789	25.4	3.37	13.28	4.4
1 Min.	0.846	24.2	3.13	12.95	4.3
2	0.788	26.0	3.37	12.98	4.3
3	0.808	27.1	3.29	12.13	4.3
5	0.851	28.6	3.12	10.91	4.3
10	0.884	29.4	3.00	10.20	4.3
15	0.787	30.1	3.38	11.23	4.3
30	0.772	32.1	3.45	10.74	4.3
60	0.867	30.9	3.06	9.89	4.3
120	0.833	35.1	3.19	9.07	4.3
240	0.771	44.0	3.45	7.84	4.2
300	0.785	40.7	3.39	8.32	4.2
360	0.751	42.0	3.55	8.45	4.2
7 Days	0.601	66.4	4.48	6.74	4.2
14	0.624	64.3	4.31	6.64	4.2

Conditions: 1% Alum
1/2% Rosin Size
Raw Water

TABLE A-XIV

Summary of PR-600-7 Calculated Results and Reaction pH Values

Time (Min.)	Scattering Coefficient	% TiO_2 Retention	% Pigment Required in Sheet for Sx=1.65	% Pigment to be Added Sx=1.65	pH of Reaction
15 Sec.	0.778	38.8	3.19	8.21	4.2
30	0.744	39.1	3.34	8.54	4.2
1 Min.	0.787	39.3	3.15	8.01	4.2
2	0.788	41.2	3.14	7.63	4.2
3	0.730	41.6	3.41	8.19	4.2
5	0.788	42.5	3.14	7.40	4.2
10	0.811	42.7	3.05	7.15	4.2
15	0.776	44.4	3.20	7.20	4.2
30	0.784	45.4	3.16	6.96	4.2
60	0.830	47.9	2.98	6.22	4.2
120	0.772	49.6	3.21	6.48	4.1
240	0.731	53.1	3.40	6.40	4.1
300	0.732	53.1	3.40	6.40	4.0
360	0.771	53.3	3.22	6.04	4.0
7 Days	0.630	70.6	3.97	5.62	3.90
14	0.599	70.4	4.19	5.95	3.90

Conditions: 2% Alum
1% Rosin Size
Demineralized Water

TABLE A-XV

Summary of PR-600-6 Calculated Results and Reaction pH Values

Time (Min.)	Scattering Coefficient	% TiO_2 Retention	% Pigment Required in Sheet for Sx=1.65	% Pigment to be Added Sx=1.65	pH of Reaction
15 Sec.	0.779	39.8	3.40	8.55	4.2
30	0.754	40.6	3.52	8.67	4.1
1 Min.	0.763	41.3	3.48	8.42	4.1
2	0.762	42.2	3.48	8.25	4.1
3	0.791	42.2	3.35	7.93	4.1
5	0.816	43.4	3.24	7.47	4.1
10	0.831	45.1	3.18	7.05	4.1
15	0.826	46.4	3.20	6.90	4.1
30	0.844	48.8	3.13	6.41	4.1
60	0.826	50.4	3.20	6.35	4.1
120	0.779	52.5	3.40	6.48	4.1
240	0.784	53.9	3.38	6.27	4.0
300	0.781	54.5	3.39	6.23	4.0
360	0.772	54.2	3.40	6.34	3.9
7 Days	0.769	60.5	3.45	5.70	3.9
14	0.717	54.6	3.71	6.79	3.7

Conditions: 4% Alum
2% Rosin Size
Demineralized Water

TABLE A-XVI

Regression Equations

Phase II - Handsheet Test Runs
Scattering Coefficient Vs. Time

Run No.	A	B x 10^{+3}	C x 10^{+6}	D x 10^{+8}	Error Estimate
600-10	0.679	0.089	3.79	2.0	0.009
600-9	0.663	0.643	1.72	-	0.045
600-2	0.635	6.023	-0.625	0.16	0.036
600-4	0.666	3.203	0.197	3.0	0.036
600-5	0.832	-1.025	2.55	-	0.049
600-8	0.820	0.149	-	-	0.038
600-7	0.771	1.054	-9.54	1.0	0.024
600-6	0.778	2.958	0.42	17.0	0.022

TABLE A-XVII

Regression Equations

Phase II - Handsheet Test Runs
Retention Vs. Time

Run No.	A	B x 10^{+2}	C x 10^{+4}	D x 10^{+6}	E x 10^{+8}	Error Estimate
600-10	26.25	-3.58	5.74	-2.65	-	0.24
600-9	28.54	5.36	-1.82	0.24	-	0.51
600-2	31.09	0.44	36.69	-356.0	8.0	1.41
600-4	35.31	15.89	-6.14	0.83	-	1.33
600-5	10.30	7.6	-8.66	3.47	-	0.43
600-8	26.41	11.3	-2.22	0.07	-	2.03
600-7	40.16	22.9	-19.37	7.09	-	1.14
600-6	41.29	30.6	-28.10	10.0	-1.0	1.06

TABLE A-XVIII

Regression Equations

Phase II - Handsheet Test Runs
Pigment to be Added (Sx=1.65) Vs. Time

Run No.	A	B x 10^{+2}	C x 10^{+4}	D x 10^{+6}	Error Estimate
600-10	15.0	19.4	-4.325	2.23	0.210
600-9	14.29	-5.4	2.652	-0.39	1.066
600-2	12.72	-13.6	11.45	-2.79	0.772
600-4	11.83	-13.6	13.16	-4.83	0.664
600-5	30.83	-21.16	31.67	-14.06	2.628
600-8	12.67	-9.35	8.269	3.06	0.938
600-7	8.05	-5.67	5.61	-2.04	0.328
600-6	8.25	-7.89	8.779	-3.47	0.393

TABLE A-XIX

Multiple Regression (PR-600-2-10)
Scattering Coefficient

Variable No.	Mean	Standard Deviation	Correlation X Vs. Y	Regression Coefficient	Std. Error of Reg. Coef.	Computed T Value
2	73.74118	114.32156	0.09194	0.00048	0.00017	2.71645
5	0.01176	1.00586	-0.69721	-0.07433	0.01028	-7.22496
6	18353.43364	37334.17977	0.03531	-0.00000	0.00000	-3.33400
9	174.93530	326.96514	0.13453	0.00004	0.00002	1.64739
11	-7.20588	136.08578	-0.18823	0.00012	0.00004	3.08316
13	0.04705	2.68108	-0.54789	0.00760	0.00370	2.05521
Dependent 1	0.74413	0.06753				

Intercept	0.73403
Multiple Correlation	0.79248
Std. Error of Estimate	0.04274

Analysis of Variance for the Regression

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Squares	F Value
Attributable to Regression	6	0.24057	0.04009	21.04926
Variable 2-Time	1	0.02914		15.95444
Variable 5-Water	1	0.29571		161.87951
Variable 6-Time x Time	1	0.01302		7.12897
Variable 9-Time x Alum	1	0.01062		5.81639
Variable 11-Time x Water	1	0.01849		10.12656
Variable 13-Alum x Water	1	0.06338		34.69915
Lack of Fit and Error	78	0.14248	0.00182	
Total	84	0.38306		

TABLE A-XX

Multiple Regression (PR-600-2-10)
TiO_2 Retention

Variable No.	Mean	Standard Deviation	Correlation X Vs. Y	Regression Coefficient	Std. Error of Reg. Coef.	Computed T Value
2	73.74118	114.32156	0.57591	0.09547	0.01065	8.95941
3	2.35294	1.26025	0.58724	16.56899	1.64623	10.06480
6	18353.43364	37334.17977	0.51512	-0.00016	0.00003	-5.20499
7	7.10588	6.55383	0.54821	-2.46554	0.31664	-7.78646
13	0.04705	2.68108	-0.36309	-1.06553	0.10922	-9.75573
Dependent 1	38.05871	8.27346				

Intercept	12.72211
Multiple Correlation	0.94946
Std. Error of Estimate	2.67783

Analysis of Variance for the Regression

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Squares	F Value
Attributable to Regression	5	5183.32911	1036.66577	144.56814
Variable 2-Time	1	4368.41016		609.19629
Variable 3-Alum	1	8521.99221		1188.43359
Variable 6-Time x Time	1	2271.56445		316.78082
Variable 7-Alum x Alum	1	6156.38282		858.53784
Variable 13-Alum x Water	1	720.87304		100.52929
Lack of Fit and Error	79	566.49133	7.17077	
Total	84	5749.82032		

TABLE A-XXI

Multiple Regression (PR-600-2-10)
Pigment to be Added

Variable No.	Mean	Standard Deviation	Correlation X Vs. Y	Regression Coefficient	Std. Error of Reg. Coef.	Computed T Value
2	73.74118	114.32145	-0.45238	-0.03454	0.00430	-8.03115
3	2.35294	1.26025	-0.48590	-6.06277	0.62139	-9.75667
5	0.01176	1.00586	0.51713	1.45553	0.24022	6.05908
6	18353.43364	37334.18759	-0.38041	0.00007	0.00001	5.76780
7	7.10588	6.55383	-0.43834	0.96821	0.11864	8.16034
9	174.93530	326.96514	-0.50774	0.00075	0.00072	1.04414
11	-7.20588	136.08581	0.24244	-0.00249	0.00096	-2.57843
13	0.04705	2.68108	0.45240	0.00957	0.08640	0.11086
Dependent 1	9.79466	2.62178				

Intercept	18.26743
Multiple Correlation	0.93223
Std. Error of Estimate	0.99741

Analysis of Variance for the Regression

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Squares	F Value
Attributable to Regression	8	501.78845	62.72355	63.04857
Variable 2-Time	1	393.46264		395.50146
Variable 3-Alum	1	817.63049		821.86718
Variable 5-Water	1	166.73980		167.60379
Variable 6-Time x Time	1	220.10418		221.24472
Variable 7-Alum x Alum	1	612.56933		615.74353
Variable 9-Time x Alum	1	27.77593		27.91986
Variable 11-Time x Water	1	18.15343		18.24750
Variable 13-Alum x Water	1	2.55879		2.57205
Lack of Fit and Error	76	75.60823	0.99484	
Total	84	577.39672		

TABLE A-XXII

TiO_2 Retention and Scattering Coefficient
PR-600-11

Time (Min.)	Scattering Coefficient	% TiO_2 Retention	Time (Min.)	Scattering Coefficient	% TiO_2 Retention
10.29	0.677	52.0	61.61	0.770	52.0
11.70	0.732	52.0	63.03	0.643	54.5
13.14	0.642	55.5	64.45	0.725	50.4
14.57	0.678	52.0	65.87	0.717	51.9
16.00	0.701	52.0	67.29	0.716	53.3
17.43	0.698	52.4	68.71	0.729	54.3
18.85	0.640	52.5	70.12	0.700	54.3
20.28	0.729	51.7	71.55	0.853	53.0
21.71	0.692	54.5	207.96	0.817	58.4
23.14	0.662	53.7	209.38	0.593	66.0
24.57	0.713	53.3	210.81	0.566	65.8
26.00	0.665	55.2	212.29	0.589	64.3
27.43	0.682	56.1	213.65	0.568	64.3
28.86	0.668	54.7	215.07	0.602	62.9
30.28	0.664	53.0	216.49	0.623	62.4
31.71	0.656	52.5	217.91	0.648	63.2
33.14	0.727	53.5	219.33	0.637	63.8
34.57	0.669	54.5	220.75	0.623	64.5
36.00	0.673	52.8	222.17	0.589	64.7
37.43	0.712	53.5	223.58	0.675	61.1
38.86	0.684	55.4	225.00	0.591	65.3
40.29	0.716	55.0	226.42	0.618	63.0
41.71	0.695	56.2	227.85	0.615	62.7
43.14	0.647	54.8	229.27	0.629	62.3
44.56	0.75	53.2	230.69	0.443	61.8
45.99	0.711	53.2	232.11	0.673	52.8
47.41	0.640	53.4	233.53	0.603	53.3
48.83	0.694	53.6	234.95	0.691	49.6
50.25	0.688	51.7	236.37	0.717	53.5
51.67	0.709	51.4	237.79	0.643	57.9
53.09	0.659	52.4	240.63	0.670	53.5
54.51	0.721	49.0	242.04	0.642	50.9
55.92	0.660	51.3	243.46	0.689	52.1
57.35	0.698	49.2	244.88	0.690	53.7
58.77	0.717	50.0	246.31	0.741	47.8
60.19	0.688	51.8			

System: 4 Alum/2 Rosin
No Recirculation

TABLE A-XXIII

TiO_2 Retention and Scattering Coefficient
PR-600-12

Time (Min.)	Scattering Coefficient	% TiO_2 Retention	Time (Min.)	Scattering Coefficient	% TiO_2 Retention
0.28	0.421	55.4	150.88	0.694	73.5
1.70	0.636	65.3	152.30	0.674	68.9
3.13	0.745	56.0	153.73	0.732	70.3
4.55	0.640	68.4	155.15	0.736	68.6
5.98	0.669	69.5	156.58	0.748	67.0
7.40	0.652	68.7	158.00	0.666	68.7
8.83	0.669	67.7	159.42	0.643	68.0
10.25	0.661	70.8	160.85	0.685	69.6
11.68	0.594	71.3	162.28	0.687	69.4
13.10	0.606	71.3	163.70	0.668	69.3
14.53	0.650	72.0	165.13	0.653	68.9
15.95	0.649	69.2	166.55	0.680	64.8
17.38	0.666	69.8	167.98	0.690	64.9
18.80	0.686	69.4	169.40	0.714	62.2
20.23	0.693	68.2	170.83	0.718	64.5
21.65	0.727	67.4	172.25	0.720	66.5
23.08	0.700	68.0	173.68	0.760	66.3
24.50	0.697	67.0	175.10	0.718	63.6
29.53	0.744	67.3	176.53	0.711	67.0
27.35	0.751	67.7	177.95	0.659	63.4
28.78	0.715	69.5	179.38	0.710	64.7
30.20	0.761	68.3	180.80	0.690	65.3
31.63	0.742	66.2	182.23	0.678	66.8
33.05	0.705	67.9	183.65	0.674	64.3
34.48	0.779	65.5	185.08	0.656	65.9
35.91	0.791	66.6	186.50	0.668	66.1
37.33	0.749	64.6	187.93	0.660	67.7
38.75	0.693	67.5	189.35	0.732	69.2
40.18	0.651	71.3	190.78	0.685	65.7
145.18	0.645	71.5	192.20	0.690	65.5
146.60	0.669	70.9	193.63	0.709	66.8
148.03	0.697	70.7	195.05	0.703	67.3
149.45	0.729	69.1			

System: 4 Alum/2 Rosin
White Water Recirculation

TABLE A-XXIV

TiO_2 Retention and Scattering Coefficient
PR-600-13

Time (Min.)	Scattering Coefficient	% TiO_2 Retention	Time (Min.)	Scattering Coefficient	% TiO_2 Retention
0.29	0.609	27.0	40.60	0.734	56.4
0.58	0.629	26.3	42.05	0.744	55.8
0.87	0.719	23.2	43.50	0.739	53.1
1.16	0.818	53.3	45.95	0.745	55.6
1.45	0.819	51.0	46.40	0.769	56.0
1.74	0.824	47.5	47.85	0.738	57.1
2.03	0.898	46.7	49.30	0.729	54.6
2.32	0.901	40.8	50.75	0.732	59.0
2.61	0.872	45.2	52.20	0.733	56.0
2.90	0.873	47.4	53.65	0.726	57.5
3.19	0.857	49.2	55.10	0.763	58.0
3.48	0.838	51.6	56.55	0.769	59.3
3.77	0.808	51.5	58.00	0.750	60.0
4.06	0.786	52.0	59.45	0.785	59.0
4.35	0.827	55.2	60.90	0.749	57.0
4.64	0.808	52.7	145.35	0.772	54.9
4.93	0.790	52.7	146.80	0.805	53.9
5.22	0.792	50.4	148.25	0.826	59.0
5.61	0.812	53.4	149.70	0.792	54.4
5.80	0.781	54.0	151.15	0.795	57.0
7.25	0.724	52.7	152.60	0.840	56.9
8.70	0.724	54.0	154.05	0.810	53.7
10.15	0.770	57.3	155.50	0.804	57.2
11.60	0.757	57.0	156.95	0.782	56.5
13.05	0.697	55.8	158.40	0.760	57.0
14.50	0.740	56.5	159.85	0.812	57.4
15.95	0.738	56.3	161.30	0.796	52.8
17.40	0.747	56.5	162.75	0.795	56.4
18.85	0.749	57.2	164.20	0.767	54.9
20.30	0.741	56.3	165.65	0.790	56.2
21.75	0.739	58.5	167.10	0.774	56.7
23.20	0.739	58.0	168.55	0.836	53.7
24.65	0.818	52.3	170.00	0.806	53.4
26.10	0.761	56.8	171.45	0.775	55.0
27.55	0.756	54.2	172.90	0.809	58.3
29.00	0.733	57.8	174.35	0.774	54.4
30.45	0.743	54.6	175.80	0.802	55.5
31.90	0.751	54.7	177.20	0.782	54.1
33.35	0.762	56.4	178.65	0.801	55.5
34.80	0.740	54.8	180.15	0.798	54.7
36.25	0.722	56.6	181.00	0.772	51.6
37.70	0.731	57.3	183.05	0.816	51.0
39.15	0.724	56.4			

System: 2 Alum/1 Rosin
No Recirculation

TABLE A-XXV

TiO_2 Retention and Scattering Coefficient
PR-600-14

Time (Min.)	Scattering Coefficient	% TiO_2 Retention	Time (Min.)	Scattering Coefficient	% TiO_2 Retention
0.29	0.495	-	40.60	0.815	77.5
0.58	0.637	-	42.05	0.793	76.7
0.87	0.690	-	43.50	0.820	76.1
1.16	0.706	-	44.95	0.790	75.2
1.45	0.687	-	46.40	0.786	77.5
1.74	0.759	72.5	47.85	0.787	76.8
2.03	0.777	75.3	49.30	0.820	77.5
2.32	0.793	73.8	50.75	0.794	77.8
2.61	0.785	72.3	52.20	0.785	77.3
2.90	0.785	73.5	53.65	0.768	76.8
3.19	0.801	77.8	55.10	0.781	77.2
3.48	0.799	76.7	56.55	0.784	74.7
3.77	0.765	75.0	58.00	0.780	75.4
4.06	0.784	76.5	59.45	0.829	74.0
4.35	0.780	76.8	60.90	0.770	76.0
4.64	0.785	75.8	214.35	0.791	72.4
4.93	0.806	73.5	215.80	0.774	72.0
5.22	0.789	75.5	217.25	0.765	72.8
5.61	0.775	79.3	218.70	0.771	71.7
5.80	0.781	78.0	220.15	0.791	65.7
7.25	0.730	77.1	221.60	0.734	73.5
8.70	0.785	77.1	223.05	0.775	71.2
10.15	0.781	78.1	224.50	0.797	72.7
11.60	0.825	79.4	225.95	0.774	71.4
13.05	0.777	77.8	227.40	0.772	66.9
14.50	0.775	74.8	228.85	0.747	70.7
15.95	0.797	76.0	230.30	0.761	71.2
17.40	0.814	77.5	231.75	0.750	68.9
18.85	0.815	78.2	233.20	0.740	73.7
20.30	0.785	78.4	234.65	0.786	71.3
21.75	0.754	74.6	236.10	0.766	72.0
23.20	0.820	76.7	237.55	0.800	71.6
24.65	0.768	74.2	239.00	0.905	55.9
26.10	0.799	73.5	240.45	0.753	68.1
27.55	0.772	75.3	241.90	0.767	70.8
29.00	0.790	74.3	243.35	0.785	69.3
30.45	0.816	77.4	244.80	0.760	70.2
31.90	0.791	74.7	246.25	0.763	74.4
33.35	0.788	76.0	247.70	0.772	72.6
34.80	0.798	74.4	249.15	0.746	70.6
36.25	0.814	76.1	250.60	0.740	68.6
37.70	0.833	73.7	252.05	0.745	69.2
39.15	0.806	74.5	253.50	0.756	67.7

System: 2 Alum/1 Rosin
White Water Recirculation

TABLE A-XXVI

TiO_2 Retention and Scattering Coefficient
PR-600-15

Time (Min.)	Scattering Coefficient	% TiO_2 Retention	Time (Min.)	Scattering Coefficient	% TiO_2 Retention
0.29	0.690	38.7	26.10	0.651	49.5
0.58	0.636	38.0	29.00	0.621	49.0
0.87	0.647	42.4	31.90	0.620	48.6
1.16	0.599	51.5	34.80	0.624	49.6
1.45	0.599	54.2	37.70	0.652	50.6
1.74	0.591	52.3	40.60	0.634	47.7
2.03	0.564	53.6	43.50	0.605	52.6
2.32	0.596	55.1	46.40	0.652	49.0
2.61	0.577	50.4	49.30	0.644	49.4
2.90	0.662	48.2	52.20	0.623	51.8
3.19	0.673	45.9	55.10	0.566	52.3
3.48	0.692	47.2	193.9	0.621	46.8
3.77	0.614	42.0	196.8	0.618	46.4
4.06	0.688	50.8	199.7	0.617	46.8
4.35	0.578	59.5	202.6	0.644	43.2
4.64	0.573	60.2	205.5	0.628	45.4
4.93	0.530	54.9	208.4	0.593	48.8
5.22	0.549	59.6	211.3	0.543	48.6
5.51	0.627	52.4	214.2	0.551	46.0
5.80	0.560	52.1	217.1	0.598	45.7
8.70	0.632	51.0	220.0	0.598	44.8
11.60	0.666	49.8	222.9	0.596	47.6
14.50	0.674	50.2	225.8	0.586	45.0
17.40	0.648	50.0	228.7	0.583	46.0
20.30	0.638	48.9	231.6	0.554	44.1
23.20	0.638	48.9	233.9	0.563	44.5

System: No Alum or Rosin
White Water Recirculation

TABLE A-XXVII

TiO_2 Retention and Scattering Coefficient
PR-600-16

Time (Min.)	Scattering Coefficient	% TiO_2 Retention	Time (Min.)	Scattering Coefficient	% TiO_2 Retention
0.29	0.673	48.0	8.70	0.771	72.0
0.58	0.640	49.5	11.60	0.783	71.5
0.87	0.668	71.5	14.50	0.781	72.5
1.16	0.726	-	17.40	0.666	66.0
1.45	0.724	-	20.30	0.788	72.5
1.74	0.703	-	23.20	0.775	71.5
2.03	0.738	89.5	26.10	0.752	74.5
2.32	0.722	88.5	29.00	0.763	70.5
2.61	0.751	85.5	31.90	0.774	69.5
2.90	0.764	84.5	34.80	0.818	72.5
3.19	0.725	78.5	37.70	0.773	72.0
3.48	0.755	77.0	43.50	0.802	73.5
3.77	0.780	77.0	49.30	0.764	75.0
4.06	0.775	80.0	55.10	0.780	69.5
4.35	0.752	75.0	60.90	0.756	70.5
4.64	0.790	75.0	66.70	0.732	75.5
4.93	0.773	74.5	72.50	0.688	74.5
5.22	0.753	73.5	78.30	0.711	76.0
5.61	0.768	74.5	84.10	0.733	76.0
5.80	0.719	70.5			

System: 2 Alum/1 Rosin
Alum Added in White Water Recirculating Line

TABLE A-XXVIII

TiO_2 Retention and Scattering Coefficient
PR-600-17

Time (Min.)	Scattering Coefficient	% TiO_2 Retention	Time (Min.)	Scattering Coefficient	% TiO_2 Retention
2.03	0.704	72.0	23.20	0.782	64.0
2.32	0.728	69.9	29.00	0.718	68.5
2.61	0.749	71.5	34.80	0.768	56.8
2.90	0.743	76.0	40.60	0.709	70.7
3.19	0.737	76.2	46.40	0.724	71.2
3.48	0.736	68.3	52.20	0.720	70.2
3.77	0.731	69.9	58.00	0.719	70.0
4.06	0.738	67.3	63.80	0.771	65.0
4.35	0.727	72.0	69.30	0.758	69.5
4.64	0.746	67.7	75.40	0.676	69.8
4.93	0.749	68.0	81.20	0.664	71.7
5.22	0.693	66.6	87.00	0.727	66.4
5.61	0.722	69.0	92.80	0.711	68.7
5.80	0.745	67.6	98.60	0.700	69.2
11.60	0.724	68.7	101.50	0.739	63.4
17.40	0.814	52.8			

System: 2 Alum/1 Rosin
Alum and Rosin Size Added in Beater

TABLE A-XXIX

Regression Equations

Phase II - Fourdrinier Test Runs
Scattering Coefficient

Run No.	A	B x 10^{+3}	C x 10^{+6}	D x 10^{+7}	Error Estimate
600-14	0.729	5.62	-119.0	7.3	0.038
600-13	0.798	-2.52	32.97	1.0	0.044
600-16	0.717	5.26	-122.0	6.9	0.035
600-12	0.582	8.12	-138.0	8.7	0.043
600-11	0.686	0.247	-1.94	-	0.053
600-15	0.617	+0.513	-51.3	-	0.039
600-17	No Correlation				

TABLE A-XXX

Regression Equations

Phase II - Fourdrinier Test Runs
Retention

Run No.	A	B	C x 10^{+4}	D x 10^{+4}	E x 10^{+7}	Error Estimate
600-14	75.90	0.00938	-1.33	-	-	1.860
600-13	43.06	1.097	-250.0	1.969	-5.0	4.632
600-16	No Correlation					
600-12	65.61	0.111	-5.89	-	-	2.941
600-11	48.87	0.392	-92.9	7.15	-	2.542
600-15	50.52	0.0208	-	-	-	4.18
600-17	73.84	-1.364	501.0	-6.24	25.1	3.51

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VITA

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